The George Fisher Baker
Non-Resident Lectureship in Chemistry
at Cornell University

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THE GEORGE FISHER BAKER
NON-RESIDENT LECTURESHIP IN CHEMISTRY
AT CORNELL UNIVERSITY

VOLUME I

Physico-Chemical Metamorphosis
and
Some Problems in Piezochemistry

by

ERNST COHEN

Ernest Cohen 1924.

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Some Problems in Piezochemistry

BY

ERNST COHEN
UNIVERSITY OF UTRECHT

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TO

PROFESSOR LOUIS MUNROE DENNIS

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PREFACE

These lectures were delivered at Cornell University during the Second Semester of 1925-1926 under the Non-Resident Lectureship in Chemistry which owes its origin to the initiative of Professor L. M. Dennis, Director of the Baker Laboratory, and which is supported by an endowment given by Mr. George Fisher Baker of New York City.

The lectures were delivered in English and were then written in German. The translation of the German draft into English was made by Dr. Ludwig F. Audrieth, and I wish here to express my very sincere appreciation of the admirable manner in which he has performed this task.

In conclusion I desire to extend to Professor Dennis and his colleagues my heartfelt thanks for their kindly co-operation which will make my stay in Ithaca one of my most delightful memories.

Ernst Cohen.

Ithaca, N. Y. June, 1926.
Baker Laboratory.

INTRODUCTORY LECTURE

QUA VADIMUS?

> "The task of an investigator requires for its success the toughness of a soldier, the temper of a saint and the training of a scholar."
>
> —HUMPHRY DAVY.

> "The philosopher should be a man willing to listen to every suggestion, but determined to judge for himself. He should not be biassed by appearances; have no favorite hypothesis; be of no school; and in doctrine have no master. He should not be a respecter of persons, but of things. Truth should be his primary subject. If to these qualities be added industry, he may indeed hope to walk within the veil of the temple of nature."—MICHAEL FARADAY.

LADIES AND GENTLEMEN: From the *Orb* which daily throws its golden rays upon this University*, came on November 14, 1925, the announcement of an anonymous gift to Cornell, the income of which is to be used for the "benefit and advancement of teaching and research in chemistry. The gift was made to enable the University to carry out a plan formulated by Professor L. M. Dennis, Head of the Department of Chemistry. Distinguished men of this and other countries in chemistry and allied fields of science are to be invited to spend one or two semesters at Cornell delivering lectures, conducting research, and generally collaborating with the Department while in residence here."

Some days later there followed the announcement: "Dutch chemist accepts offer to teach here." Let me assure you that I feel very much honored by your kindness in choosing me as the first incumbent, and that I fully realize the duties laid upon me by your doing so. I sincerely hope that this establishment of the new "Non-

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* *The Cornell Daily Sun.*

Resident Lectureship" may, as the years go on, bring the results that were in the mind of the anonymous benefactor when he made this generous gift to Cornell.

When, for about a quarter of a century, a man has, day after day, devoted himself to university instruction, has seen numerous generations enter the Temple of MINERVA, and has seen them leave her sanctum decked with the doctor's hood, when he has passed those years in unbroken and intimate intercourse with his pupils, it is obvious that he is perfectly well acquainted with the difficulties which many of them have met on their way.

QUA VADIMUS? WHICH WAY SHALL WE GO? How are we to arrange our studies? This is the question which year after year many new students ask themselves when they enter the gates of the university, and not only themselves, but also their older colleagues, or the professors to whose guidance they are going to entrust themselves, for in most cases it appears that they themselves are unable to answer this question satisfactorily.

How could it be otherwise? For do they not take a road totally different from the one they have trod up to this time, are not the requirements totally different now that they are no longer under rigid scholastic restraint? Is it any wonder that they are in the position of the medical practitioner who standing at a sick bed is often confronted with the problems of solving an equation with thirty unknown quantities? The demands which society will make of the beginner in the execution of his scientific profession are such that only he can hope to satisfy them who knows how to use in the most practical way the time allotted to him for study and for scientific development. Means to attend this end—lectures, practical class-work, books, colloquia, students' lectures, excursions,—are not wanting in these days; on the contrary, there is rather "*embarras de choix*", but the difficulty for the future scientist is to choose rightly, at the proper moment, and after the choice, he must solve the question: "In what way can I make the most practical use of the means that are presented to me?"

Let us pass in review the whole machinery of instruction and indicate the importance and meaning of every part, while at the same time we answer the question how to make the best use of these parts. And let us bear in mind that the student's "Lehr- und Wanderjahre" should make him not only a scholar, but especially a "man."

"Die Vorlesungen sind eine unangenehme Unterbrechung der Ferien"* is a well known complaint uttered by professor and student alike, but let us not forget that these are at least of *some* use. Purposely I say "of some use" for experience teaches that the student is apt to overrate the significance of lectures. Enter the lecture room when the students, eager for knowledge, are assembled there, and you will conclude from the continual scratching of pens, which indicates that the words of the professor are perpetuated on paper, that "taking down verbatim" is considered to be a highly important part of the curriculum. Times have changed. Seventy-five years ago the renowned Dutch author KNEPPELHOUT published his "College Life", a book well worth reading even now, in which with caustic irony he divides the professors into two classes: the dictating professors, and the teaching. He berates the former roundly, because they compel the young man of twenty to keep up with the erratic rate of the glib lips, without allowing him time to let his brains catch their line of thought. Nowadays it is the student who seems to attach such an immense importance to taking down the words he manages to catch. The more experienced student wonders if short notes worked out as soon as possible after the lecture would not answer the purpose much better, with the simultaneous use of text books to which he is so often referred. Would not this lead to a great saving of time? By this method he would avoid the one-sidedness which is a common error of the student in taking the professor's exposition as the only correct and the only possible one. In this way the student easily escapes the rock of "jurare in verba magistri" which is so dangerous, especially to the beginner.

Moreover, the use of good books when working out what he has heard in the lecture room offers the great advantage that the student gets a better insight into the real value and the significance of a lecture in general.

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* "The lectures are an unpleasant interruption of the holidays."

The subjects are discussed from the professor's subjective point of view as regards the importance which ought to be attached to certain special parts of the science he teaches. Thus it may happen that more attention is paid to subjects to which the professor has especially devoted his energies than to others, no less important, which are farther removed from his special field of investigation. The text book will draw the student's attention to the existence and importance of such subjects, perhaps acquaint him with problems which captivate him more strongly than those of which he heard in the lectures. And in this way he enters, as it were imperceptibly, the domain of independent study, the study which distinguishes the University from the schools he has just left.

I hear one of you object: "Yes, all this is very fine, but in the examination we are required to know all that has been treated in the lectures. "Then my reply is: "Undoubtedly there are lectures, especially those given to freshmen, in which the elements of a certain science are presented, and it is absolutely necessary for every one who wishes to go deeper into this science to be well acquainted with all that is treated in the lectures. But this is true of a few courses only. It is absolutely untrue for advanced students, and for these a deeper insight into, and a broader view of, the matter is of the greatest importance. No reasonable teacher will ever insist that his pupils pay most attention to those parts of science which he has treated exhaustively in a course of lectures. The purport of these lectures is to fix the student's attention on important points, to acquaint him with the literature which has been published on that particular subject, to point out the way in which certain problems may be studied in connection with the present advance of learning, and, in the last instance, all this is intended not only to make him acquainted with those problems and the way of solving them, but especially to awaken his love for the study of other topics which have not been treated, and so to fit him for the solution of new problems. I am sure that you will agree with me when I say that this end cannot be attained by mastering only that which is taken down in the lecture room. I can give you a striking example. When studying thermodynamics, many students, I may say most, are satisfied with studying the derivation of the numerous relations which the lecture teaches them. When they have to apply the formulas thus derived, we are immediately aware that they are not able to do so, especially in the computation of concrete cases. Only by continual practice in the solving of problems is it possible to get a clear understanding of the subject.

But again I hear the objection that this method of study would take up too much time, that those who wish to complete their university course within a reasonable period have not sufficient leisure for such practice. Allow me to set your mind at ease on this point. The man who takes up his studies in this way saves a lot of time. The thorough method is far superior to the superficial. It is true that at first the beginner will think that he makes little headway, but this impression is entirely wrong and soon disappears. The numerous, disheartening repetitions which are the lot of those who are less conscientious are eliminated in this way. The Italian proverb obtains here also:—Che va piano, va sano, e va lontano.*

Practical class work, if judiciously ordered, forms a pleasant and powerful help to stimulate the studies at the writing-desk which, especially at first, are more or less monotonous. Many generations of students have experienced this since JUSTUS VON LIEBIG insisted on practical classwork as an inherent part of the chemical study. He put this idea in practice at his celebrated laboratory at Giessen. As early as 1683, JOHANN MORITZ HOFFMANN, professor of medicine at Altorf, had expressed the same idea. And today we may make PASTEUR's words our own: "Les laboratoires sont les temples de l'avenir, de la richesse et du bien-être; c'est là que l'humanité grandit, se fortifie et devient meilleure."†

I just now used the phrase "if judiciously ordered". This is true for the teacher who must make the best choice out of the heap of material that lies ready to hand, as well as for the students as regards the manner in which they make use of the opportunities which are offered them.

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* Who goes slowly, goes wisely and goes far.

† The laboratories are the temples of the future, of wealth and well-being; there mankind grows, gains strength and progresses.

In connection with the high educational value which a correct method of practical class work possesses, I will enlarge on this point for a moment. "Ce n'est pas assez de savoir les principes; il faut savoir manipuler."* No less a person than MICHAEL FARADAY took those words for his motto when he published his first manual of practical chemistry, "Chemical Manipulation, being instructions to students in chemistry on the methods of performing experiments of demonstration or of research with accuracy and success." For many decades the great importance and the deep significance of this "savoir manipuler" has been recognized all over the civilized world, and today this principle is everywhere introduced in our teaching of the non-mathematical sciences. Therefore, it may appear to be unnecessary to point out once more that for the prospective natural philosopher it is of the utmost importance to apply himself, heart and soul, to this branch of his studies. Yet experience has taught me that, especially at the beginning, most students do not realize this obvious truth. Furthermore, whoever thinks that a working day of eight hours will be sufficient for him to attain his purpose, let him desist from the study of the exact sciences and choose a sphere of activity in which the number of working hours is regulated by law.

Every chemist must be skilled in recognizing and detecting the substances which he handles every day, that is, in qualitative analysis, and it stands to reason that he must also be thoroughly familiar with the methods which acquaint him with the quantitative composition of those substances. Whatever career he will follow afterwards, he must have mastered the A. B. C. of these methods. It seems commonplace to enlarge on these points, but my excuse is that more than once I have met students who were strangely deficient in their knowledge of analysis. I willingly admit that there is a certain monotony in making oneself familiar with these manipulations, that for many it is "making the best of a bad job", but it is an absolute necessity.

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* It is not sufficient to know the principles: manipulation must also be mastered.

Then we should not forget that performing analytical operations offers an excellent opportunity of training oneself in keen observation, in accuracy, and last but not least, in economizing time. He who is able to perform a number of analyses simultaneously and to divide his time in the most practical and economical way, acquires qualities which are of great use to him in future years in every branch of study. He learns to make the most of his time. We cannot enter into further particulars about this point, but I wish to call attention to a serious mistake which is very common and which often leads to a highly undesirable waste of time and material. Many students, after a quantitative measurement, put off the calculation of the results until after a second experiment. Now this is most unwise, for often the calculation shows that some error has been made, and if this error had been known to the student before the second experiment had been carried out, he would have been warned in time to avoid the rock on which his first experiment had stranded. For the serious worker, "manipuler" has another great advantage: it compels him to bear continually in mind the principles on which his work is based, and to recall and put into practice that which he has heard in the lecture room, or read in his books. This advantage, however, is only for him who does not work mechanically, or does not blindly follow the manuals he uses in the laboratory, without verifying the laws they teach.

The memorable words of CLEMENS WINKLER should be engraved over the entrance of every chemical laboratory, and not only there, but also in the mind of every student of chemistry: "Die wirklich erfolgreiche Durchführung anorganisch-chemischer (I add: organischer und physikalisch-chemischer) Arbeiten ist aber nur demjenigen möglich, der nicht allein theoretischer Chemiker, sondern auch vollendeter Analytiker ist, und zwar nicht nur ein praktisch angelernter mechanischer Arbeiter, sondern ein denkender, gestaltender Künstler, vor dem jede der durchgeführten

Operationen in theoretischer Klarheit liegt, dem die Stöchiometrie in Fleisch und Blut übergegangen ist und der bei allem, was er tut, von ästhetischem, dem Sinne für Ordnung und Sauberkeit, vor allem aber vom Streben nach Wahrheit geleitet wird."*

But too often the student feels inclined to complete the course which has been set for him in the shortest time possible, without realizing that the way in which he completes his task must be considered as of the greatest importance as regards his further attainments. He often shows little desire to repeat an unsuccessful experiment, and does not appear interested in trying to better his results. And more than once we hear from those who wish to explain their lack of perseverance this excuse: "I prefer the theoretical side of chemistry to the practical."

The inclination to withdraw from experimental work in favor of speculative philosophy, to the great detriment of the scientific faculty, is especially noticeable in those students who early in their university career take up the study of philosophy. If the teacher of chemistry succeeds in convincing them that they are on the wrong road, and that a continuation of their scientific studies will give them equally great gratification, such episodes, when after a shorter or longer time the difficulties are vanquished, generally result in the student esteeming himself fortunate that he succeeded in checking his speculative inclinations at the proper time.

On the strength of these experiences I venture to warn against a premature study of speculative philosophy. If the natural philosopher, when he has won his way in scientific fields, feels inclined to enter the domain of speculative theories, he still may find an opportunity of following MEPHISTO's advice:—

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* Successful inorganic-chemical (I add: organic and physico-chemical) investigations can only be carried out by such men as are not only theoretical chemists, but also perfect analysts, not only artisans with practical routine training, but thinking, plastic artists who have a deep insight into the theory of their experiments, who have stoichiometry at the tips of their fingers, who are always led by an aesthetic spirit for order and cleanliness, but above all by a desire for truth."

"Mein teurer Freund, ich rat' Euch drum
Zuerst Kollegium Logikum
Da wird der Geist Euch wohl dressiert,
In spanische Stiefeln eingeschnürt,
Dass er bedächtiger fortan
Hinschleiche die Gedankenbahn,
Und nicht etwa die Kreuz und Quer
Irrlichteliere hin und her."*

Then his critical judgment will enable him to turn to good advantage all that can benefit him in his further study in mathematical sciences.

Another possible error, of a totally different nature, is, that he who devotes himself to practical laboratory work may have no eye for anything but his own experiments. The fact that in a laboratory a number of neophytes and more advanced students are at work together, on different, often totally divergent experiments, gives all of them an opportunity of paying attention not only to their own work, but also to the work of their fellow students, of seeing and hearing what others do, and of profiting by the mistakes and failures of their neighbors. It is a great advantage for the students if varied kinds of experiments are carried out in the same laboratory; the tendency nowadays, in some university laboratories, to restrict the investigations to a narrow field is therefore not to be recommended.

No one can deny that the path of the prospective natural philosopher is beset with difficulties, or that he will meet with numerous reverses. But difficulties have their use; they stimulate the desire to overcome them. Thus the study of exact sciences exercises a beneficial influence on the formation of character in those who apply themselves to it with untiring zeal. The difficulties which the student must conquer steel his patience, and develop his perseverance and his self-reliance, and when at last he has attained his end, he enjoys the peculiar satisfaction which indemnifies the genuine investigator for the most difficult labor and the greatest exertions. An advantage that can hardly be estimated at its true value is that such endeavors develop the sense of truth in a man. Has not the Swedish pastmaster in chemistry, BERZELIUS, declared: "Der erste und grösste Ruhm eines Forschers besteht in seiner Wahrhaftigkeit und Gewissenhaftigkeit; gegen diese gehalten, verschwinden alle wissenschaftlichen Verdienste."*

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* "For this I counsel my young friend
A course of logic to attend;
Thus will your mind, well-trained and high,
In Spanish boots stalk pompously;
With solemn look and crippled pace,
The beaten road of thought will trace:
Nor here and there, through paths oblique,
In devious wanderings idly strike."

You see that a natural philosopher must have no mean qualifications if he wishes properly to perform the work he has undertaken. There are more and other qualities he must possess if he wishes to escape disappointments, but I cannot enter into further details here. If you wish to go deeper into this subject, I refer you to the "Consolations in Travel or the Last Days of a Philosopher" by HUMPHRY DAVY, written down about a hundred years ago in his journey through Europe, and I advise you to read the fifth dialogue, which contains truths no less pregnant in 1926 than when they were set forth by the great British chemist.

We now turn to the third group of aids to the student, books of study. I think first of all of the question, "What text book shall I use?" For the beginner I can recommend the use of one special text book, so that the student gets acquainted with the elements of the science to be studied. But he should, as soon as possible, pass to the study of special subjects in special books. The choice is unlimited; the enormous increase of literature all over the world requires different subjects to be treated in monographs. Very often the scientist is obliged to turn to books written in some foreign language. This is, however, a great advantage to the student whose knowledge of foreign languages is generally below par, for it obliges him to go deeper into the study of these languages, and by using these books, he develops greater linguistic proficiency.

The man who, later on, wishes to make the results of his researches known to a greater number of readers, should be thoroughly conversant with one or more foreign languages. But in whatever language the text books the student uses may be written, he should first of all learn to read with accuracy. The great majority, and experience has shown this very clearly, have had insufficient training in their earlier schooling. From what precedes, it follows that a library, however small it may be at first, is a "conditio sine qua non" for the earnest student. But inquiries on this point have taught me that the length of the bookshelves of most students cannot be reckoned by meters, but by decimeters at most. If the student cannot consult his own library, serious study is handicapped for many reasons, one of which is loss of time if he has to borrow the books he needs.

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* The first and greatest glory of an investigator is his truthfulness and conscientiousness; all his scientific attainments are eclipsed by these qualities.

The man who possesses a library of his own will have a better opportunity of studying chapters which for the moment are of no immediate use to him, and in this way he enlarges his views and his knowledge. I cannot insist too much on the necessity of the student forming a library at his earliest convenience. He will never rue the money he spends on it. In this library he should find a place for books which treat on the history of science, as well as for those which I should like to call the "belles lettres" of science.

"Historische Studien gehören sehr wesentlich mit zur wissenschaftlichen Erziehung."* ERNST MACH, with many others, has not only drawn attention to this fact, but suiting the action to the word, has left us many an essay which bears witness to the truth of this statement. The man who studies the history of science will get a better insight into the problems that are nowadays a centre of interest, nay, he will also be convinced that:

". . . es ist ein gross Ergötzen,
Sich in den Geist der Zeiten zu versetzen,
Zu schauen, wie vor uns ein weiser Mann gedacht."†

And when he reads the biographies of those "wise men" in which are described the ways in which knowledge was obtained, and in which the obstacles are shown which had to be conquered, he will learn to think humbly of himself and not overrate his own accomplishments. A large number of chemical and physical works are at his disposal in which great men, such as AMPÈRE, ARAGO, BERTHELOT, BIOT, LUDWIG BOLTZMANN, CHEVREUL, DAVY, FARADAY, VON HOFMANN, JUSTUS VON LIEBIG, EDMUND O. VON LIPPMANN, ERNST MACH, VICTOR MEYER, RAMSAY, SCHÖNBEIN, TYNDALL, to mention but a few, have treated subjects, in or even outside the pale of the science they studied, in essays which excel in beauty of form and depth of thought, and grip the attention of the reader by the striking way in which they confirm FRANÇOIS ARAGO's words: "La culture des sciences fortifie l'intelligence sans détremper les ressorts de l'âme, sans émousser la sensibilité, sans attiédir aucune des bonnes qualités dont la nature a déposé le germe dans le coeur humain."*

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*Historical studies are part and parcel of a scientific education.

†". . . 't is delightful to transfuse yourself
Into the spirit of the ages past;
To see how wise men thought in olden time."

Great importance must be attached to the colloquia and student-lectures. The intention of the former is to encourage the advanced student to take cognizance of the latest results of science, and give him an opportunity to state his own views on the subjects which have more particularly drawn his attention. Thus he is obliged to acquaint himself at the same time with what was previously accomplished in this direction. If the prospective investigator wishes to be conversant with the progress of science, if he wants to know what problems are of actual importance, he must read one or more of the numerous periodicals which will inform him on this point and in which, at the same time, he can follow the evolution of science in cognate or more distant domains. The cardinal point of such studies is the fact that the student gets acquainted with the literature, that he learns to find his way in it, that he gains information about problems of which hitherto he was quite ignorant. In his later life he will often be required to find his way in a field of science where, up to that moment, he had never set foot. To prepare him for such contingencies is the first aim of the colloquia. The reading of his short paper trains him in logical formulation of ideas which continual practice only can give. This is of great profit to the man who chooses a scholastic profession, but no less to the manager of some industry who comes in contact with many persons of varying intellectual faculties to whom he must explain his ideas.

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* The pursuit of science strengthens the intelligence, without weakening the energy, without blunting the sensitiveness, without chilling any of the good qualities the germ of which has been placed in the human heart by Nature.

The student-lectures too aim at the development of the same qualities. Here the student is required to give his audience an insight, either into an up-to-date problem of which he has made a special study, or into some problem of earlier times. The preparation of such an essay, the reading of which according to the well-tried prescription by Faraday, should never take longer than one hour, acquaints the prospective lecturer with the literature of his subject. Let him never forget to consult "in originali" the books which refer him to the subject matter in hand, neither when he prepares his paper for the student-lecture, nor when later on he publishes his investigations. He should never trust abstracts made by others, for many an investigation has been rendered totally worthless from the very outset because the author, a victim to indolence, had disregarded this precept. In the student-lectures, as well as in the colloquia, every one derives profit, not only from his own essay, but also from those of his fellow students, while the discussion on the subject widens their minds.

The first aim of the man who chooses the University as the place where he prepares for later life, should be to get an all-round training in the science which he wishes to study. He does not always know what path he will choose when the gates of the university shall close behind him. Is he going to follow a scholastic profession, or a technical, or will he devote himself to a life of purely scientific study? It often happens that some predilection reveals itself during his stay at the university, and that in those years a fitness for some special career manifests itself. The great thing therefore is that his university course should be such as to allow him to defer for a time definite choice as to his subsequent career.

When we take all this into consideration, it would be very convenient if the university curriculum contained another item, viz. excursions. By visiting and viewing certain chemical works the student gets a notion of the value of the applications of science. I say a notion, for he must not overrate the value of such excursions. From their very nature they can give him only a somewhat vague idea of different industries. Their complicated nature, the short time which can be allowed for such visits, the secrecy which envelops, and very rightly, the plants visited, make a deep study of the matter an impossibility, even if the student has prepared himself by reading up books on the subject. It is of course a totally different matter if the prospective *doctor chemiae* can become acquainted with an industry by working in a plant for some time; a stay at a laboratory where special investigations are carried out (I have in mind the laboratories at some factories, as well as government agricultural stations and the like) can form an important element in his scientific training insofar as in such surroundings quick and accurate work is necessary. I need not point out that excursions as well as a prolonged stay at some factory can be of use to the more advanced student only.

Traveling during the university course in his native country would have many drawbacks, but when once the student has obtained his degree he must be enabled (at any rate the more talented) to go on an educational tour. Even if a prolonged stay in a foreign country should have no other effect than that the young doctor acquired fluency in the language of this country, the allowance granted would be well spent. For him who has eyes to see and ears to hear, the advantages of an educational tour abroad are of incalculable value for his whole life. He is stimulated by the study of new methods of investigation, by coming into contact with younger men of another nationality whose ideas and sentiments are different from his. New relations and new friendships are contracted, perhaps for life. The man who has gone through such a period never gets tired of dwelling on the advantages and the pleasant memories he has kept of that time. And when he returns to his own country, after a stay in some centers of learning, he recognizes the truth of the old adage: "As many languages a man speaks, so many times he is a man."

The plan which I have sketched here will be of benefit to our "itinerant" students, but no less to the laboratories they visit. Great is the influence which "outsiders" can exercise on the work in a laboratory. Their presence is an excellent remedy against the "humdrum routine" of the students, and the "fads" of the professor.

When the student has taken his first degree, he enters upon the most instructive period of his studies, that is, if he wishes to conclude his college life with a doctor's degree. Up to this moment the examinations, though conducted in a very liberal and fair spirit, have exercised a certain constraint upon the study of the prospective doctor. Now, however, he can give his whole mind to a subject of his own choosing. This stimulates his energy, his perseverance; he is obliged to study the literature which bears upon his subject, and when at last he has completed his research, he must put his results into readable shape, and work them up into a logical sequence, and all this is excellent training in the art of putting his thoughts to paper in a lucid and accurate form.

Let no one imagine that the course which I have sketched leads to the moulding of a scientist who satisfies every requirement of science or society. This is by no means the case. Remember that in the first part of this discourse I pointed out that the "Lehr-und Wanderjahre" of the student should make him not only a scholar, but also a man. I hope that I have made it clear that the way which leads to the forming of a scholar possesses more than one factor which can also play an important part in the forming of a man. The importance of other factors, however, should not be undervalued.

"Es bildet ein Talent sich in der Stille,
Sich ein Charakter in dem Strom der Welt!"*

The man who devotes himself exclusively to study, who keeps aloof from an environment such as only the University can give, who does not try to set his knowledge and gifts on a broader foundation by an intercourse with "all sorts and conditions of men", who does not try to give form and tone to his character, is wanting to himself and to society. Only by mixing with the different sets at the University does he find opportunity to exchange thoughts with fellow students whose intellectual horizon is quite different from his own: only thus will he guard against those qualities of self-consciousness and one-sidedness which can but harm him in later life.

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* A man of talent is formed in seclusion, a man of character in the whirlpool of Life.

Is it not a distressing sign of want of culture when among students who already have spent some years at the University, and have passed examinations there, some are found who do not know what the NOBEL prize is, or who do not know even the names of those of their countrymen who have made themselves a great name in the science which these students have chosen for their own study? There is no better place for the prospective natural philosopher to learn that his subject embraces but a very small part of human knowledge than among the fellow-students of different faculties, and so he will be prevented from becoming overwise in his own conceit. In associations and debating clubs he finds another and perhaps a better opportunity of putting his thoughts lucidly and concisely into words. The discussions with others whose conceptions and opinions differ from his, train him in self-command. Here is the arena where he prepares himself for life's struggles which await him after his college years. Here he finds an opportunity to develop the qualities which, together with his scientific attainments, will have such a great influence on his future happiness.

As early as the middle of the last century the Dutch author KNEPPELHOUT, whom I mentioned at the beginning of my discourse, justly made sport of the man who in later years should write a pompous and learned and necessarily Latin work: "De methodo studendi optimo".* It has not been my purpose to give you such a manual, for I am of the same opinion as the author of "College-Life". There is no hard and fast rule which tells you how to become clever. There are more ways to the wood than one; in our case the special qualities of the individual are of the greatest importance in the choice of the way. It has been my aim to

*On the best Method of Studying.

point out to you some paths which lead to the same goal. The paths differ from one another, but every one is free to take the road he likes best. But whatever path you follow, try to remember that it is always a steep mountain-road, the ascent of which is difficult, and that you will reach the top only if you exert yourself to the utmost. In so doing you will fulfill the hopes expressed by Andrew D. White, first President of this University, carved on the granite Gateway presented by him to Cornell:

> "So enter that daily thou mayest become more learned and thoughtful
> So depart that daily thou mayest become more useful to thy country and to mankind."

PART I

PHYSICO-CHEMICAL METAMORPHOSIS

PHYSICO-CHEMICAL METAMORPHOSIS

FIRST LECTURE

IN THESE lectures we will concern ourselves with the *Physico-chemical Metamorphosis of Matter.* You are probably cognizant of the fact that the word *Metamorphosis* is derived from the Greek *μεταμορφοῦν* meaning "to transform." The question whether a definite chemical substance may exist in a number of forms or modifications (Polymorphism) has been keenly discussed for more than one hundred years.[1]

Even after Smithson Tennant[2] had shown in the year 1796 that the diamond "consists entirely of charcoal, differing from the usual state of that substance only by its crystallized form," it was the opinion of Humphry Davy[3] that "Bodies cannot be exactly the same in composition, or chemical nature, and yet totally different in their physical properties." Not until he had convinced himself of the correctness of Tennant's observation, when in the year 1814, incidental to a journey on the Continent, he had, in Florence, actually burned a diamond by means of the sun's rays, did he accept the other view. But even after Eilhard Mitscherlich[4] had noticed the existence of polymorphic modifications in the case of sulphur and a number of other substances, the appearance of this phenomenon was regarded as exceptional. Pasteur[5] expressed himself as follows: "Le nombre des substances dimorphes (polymorphes) est encore très restreint. Il est probable qu'il s'accroîtra beaucoup à l'avenir, surtout lorsque l'on aura determiné complètement les formes de toutes les combinaisons des laboratoires." Further discussions will bring out the truth of Pasteur's prophesy. At the present time we recognize thousands of polymorphic substances and almost every day serves to bring new examples to our notice.

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[1] A detailed survey of the extremely interesting history of Polymorphism may be found in the first chapter, edited by A. Arzruni, of the third volume of *Graham-Otto's Lehrbuch der Chemie*. Braunschweig 1898.

[2] *Phil. Trans. Roy. Soc. London*, 1797, 123.

[3] *Phil. Trans. Roy. Soc. London*, 1814, 557.

[4] *Ann. chim. phys.*, **19**, 407 (1821).

[5] *Ann. chim. phys.*, (3), **23**, 269 (1848).

In my presentation of this subject, I will endeavor to make clear what external conditions, temperature, pressure, solvent, etc., will induce the formation of new modifications of substances already known, and the consequences of the existence of one and the same substance in a number of forms.

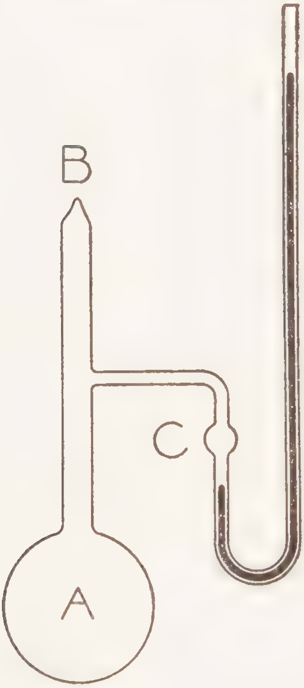

FIG. 1

In order to place before you the subject matter with greater clarity it may be well to take up a few facts with which you are undoubtedly acquainted. If a volatile liquid, such as water, is placed in a glass flask *A*, Fig. 1, to which is fused a manometer *C* that contains mercury, and if the flask is then warmed to various temperatures in a thermostat, the pressure of the vapor as indicated by the manometer will, as everyone knows, vary with the temperature. We may conveniently represent graphically the pressures measured at various temperatures. For this purpose we may plot our results by means of the Cartesian co-ordinate system, in which the abscissae represent the temperatures, and the ordinates the corresponding pressures expressed in mm. of mercury. In this manner we obtain the points *a*, *b*, *c*, *d*, and *e*, Fig. 2, which express the pressures of the water vapor at the corresponding temperatures. If now we connect these various experimentally determined points by a continuous line, the curve obtained represents the vapor pressure curve of water. If we continue the experiments below *P*, we obtain the points *h*, *g*, and *f*. If these points be connected by a continuous line it will at once become apparent that this curve does not represent an extension of *ea*, but that we have here two different curves which intersect at the point *P*. A closer examination of the contents of the flask *A* will reveal the fact that below the temperature corresponding to the point *P*, water is no longer present in the flask *A* as a liquid, but has changed into ice. The temperature corresponding to the point *P* is found to be 0°. Whereas the curve *Pae* represents the vapor pressure curve of *liquid water*, the line *Pf* deals with the vapor pressure of *ice*, that is, the vapor pressure of a solid substance. This is termed the Sublimation Curve. The fact that solid substances as well as liquids have vapor pressures should be well known to you from examples which we meet in our daily life. Consider the case of naphthalene which we use for purposes of disinfection. If one allows a piece of this substance, a solid at ordinary temperatures, to lie exposed to the air, it will gradually lose in weight because of the vaporization which is taking place, and it will finally disappear.

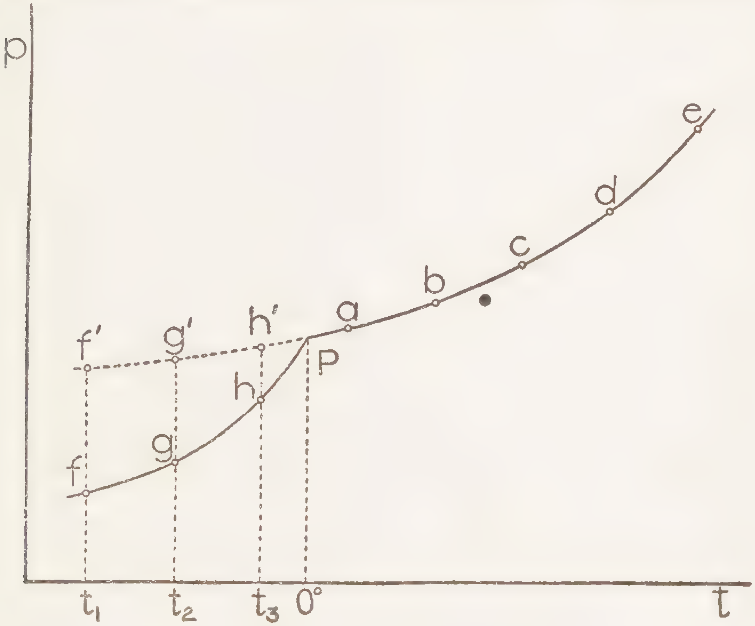

FIG. 2

However, under certain conditions substances may behave in a manner different from that just described. If water is cooled in the flask very carefully below 0° it may happen that freezing does not take place. Then we say that the water is *undercooled*. The experiment yields in this case the points h', g', and f' for the vapor pressure. If these points be connected by a continuous line, the resulting curve represents the vapor pressure curve of undercooled water. At the corresponding temperatures the water exists in an unstable condition, and that state of affairs may be expressed by the term "*metastable*". From the curve we can see that at a given temperature the vapor pressure of this "metastable" water is higher than that representing it in a stable condition (ice) at the same temperature. At the point P, the intersection of both vapor pressure curves, the vapor pressures of ice and water are the same; that is, ice and water are in stable equilibrium at the temperature corresponding to the point P, 0°. If we bring into contact with the undercooled water at the temperatures corresponding to the points h', g', f' . . . some of that phase which is stable at those temperatures, namely ice, stabilization soon takes place. The undercooled water is transformed into ice; it is frozen.

We can express the same observations in another way. If liquid water is cooled below zero, it is transformed into ice, whereas ice when warmed above this temperature is converted into water. We are met here by an example of *reversible* change. The temperature at which this transformation takes place may be called the *transition temperature* of water (ice), and may be represented by the equation,

$$\text{ice} \overset{0^\circ\text{C.}}{\rightleftarrows} \text{water}$$

insofar as the latter expresses our results considering only the existence of the stable phases. At the same time we must not forget that this transformation may undergo retardation under certain conditions and that because of this fact we may run over into a region of temperatures representing metastable conditions. The transition temperature, in this case 0°, we may define as that temperature at which both forms of the substance H_2O, ice and water, may coexist in stable equilibrium. Incidentally it might be mentioned that this temperature generally undergoes a variation depending upon the external pressure applied to the substance. We will later come back to this point.

Let us now perform a different experiment using the apparatus shown in Fig. 1. We will place a solid substance *S* in the flask and, as in the previous case, determine its vapor pressure at various temperatures. The fact that the vapor pressures may be extremely small, even at high temperatures, is not of prime importance; any resultant difficulties which might be encountered can easily be eliminated with the present refinements for the measurement of pressures now at our disposal.

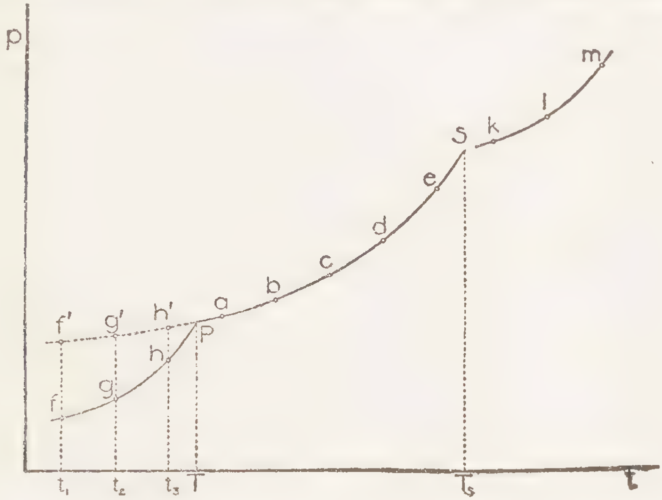

Fig. 3

Proceeding from lower to higher temperatures we again obtain in a simple case (more complicated examples will be discussed later) two vapor pressure curves *f*, *g*, *h* and *a*, *b*, *c*, *d*, *e*, Fig. 3, which intersect in the point *P*. If the substance existing at pressures corresponding to the points *f*, *g*, and *h*, be examined, as well as that existing in the apparatus at pressures corresponding to the points *a*, *b*, *c*, *d*, and *e*, it will be seen that the two bodies are not the same in both cases, despite the fact that their chemical composition has not been altered. They will be found to differ in their crystalline form. To distinguish these two modifications of the substance S, we may designate them as the α and β forms respectively. We will name that substance whose vapor pressures correspond to the points f, g, h . . . the α form, whereas that modification whose vapor pressures are indicated by the points a, b, c, d, and e, we will term the β form. The two curves intersect in the point P, where the vapor pressures of the α and β modifications are equal; at the corresponding temperature T, the two forms are in stable equilibrium with each other. The phenomena which we notice here are quite analogous to those which we learned to recognize in the transformation ice ⇆ water. Thus, if the α modification be heated above the temperature corresponding to the point P, namely T, it will change over to the β form. Reversely, if the β form be cooled below $T°$, it will disappear and the α modification will become existent. The temperature T may again be designated as the *transition temperature*. Likewise, the reactions which have taken place may be represented by the equation,

$$S_\alpha \overset{T°}{\rightleftarrows} S_\beta$$

in which the two arrows indicate the fact that we are dealing with a reversible change.

If the α modification be warmed above the transition temperature T, until all of it has been converted to the β form, and if this latter substance be very carefully cooled below the transition temperature, a phenomenon may arise which is quite common and which we have previously discussed on page 22; that is, the β modification may undergo no change and the substance may remain in that form when cooled below the transition temperature, instead of changing into the α modification. Such conditions may adequately be represented by an extension of the curve e, d, c, b, a, P in a direction as indicated by the points h', g', f' . . . which represent the vapor pressure of the β modification in a metastable state. The vapor pressures of the metastable phase are higher than those of the α form. If the metastable β modification be brought into contact with a very small quantity of the stable α form, (analogous to seeding to cause crystallization from solution to take place) the stabilization velocity of the β form will be greatly accelerated, so much so, that after some time the β material will have been changed entirely to the α form. The addition of small traces of a solvent which will dissolve *S* will generally cause stabilization to take place more quickly; very often it will multiply the speed of transformation a thousand times. Later we will learn that this retardation in changing to the stable form is quite a common occurrence among polymorphic substances. Many of the phenomena which they present have remained for a long time unknown, because of the pertinacity of this retardation.

Following the proposal of Otto Lehmann we will designate as *enantiotropic* those substances, such as *S*, which exhibit a transition point, above which the β modification and below which the α forms are, respectively, the stable forms. The phenomenon itself we will term *enantiotropy*. As we have seen, the transformation of enantiotropic substances is of a *reversible* nature.

It may be pointed out that if we allow the temperature of the β modification to rise, the melting point will be reached. The resulting liquid, the molten form of the substance *S*, has a very definite vapor pressure at any given temperature, viz. the points *k*, *l* and *m*. If the experimentally determined points *k*, *l*, *m* . . . be connected by a continuous line, the line will represent the vapor pressure curve of the molten substance *S*. Since only solid phases will be discussed in this case and in the following ones, for only solids are capable of existence in polymorphic modifications, we will not consider the vapor pressure curve of the liquid phase beyond this point.

We will now take up a very definite and typical case of an enantiotropic substance, one which will enable us to visualize more clearly the facts and consequences of enantiotropy. This substance is tin. Permit me to direct your attention to a number of facts regarding this metal which have long been known and discussed. In 1851, O. L. Erdmann[6] published a paper in which he described a structural transformation of this metal as he had observed it in the case of some organ pipes from the old castle church at Zeitz. Offering a possible explanation he is quoted as saying that the change "was probably due to the vibrations to which the metal of the organ pipes had been exposed."

This fact remained unnoticed until 1869 when Fritzsche[7] again called the attention of the scientific world to it. He describes his experiences and observations as follows:

"The chief of a commercial firm informed me in February, 1868, that many blocks of Banca-tin, belonging to the same consignment, had decayed in the store of the custom-house. I remembered dimly that some years previous a large number of cast-tin buttons for military uniforms which had been kept in one of the Crown magazines had been found to have decayed into a shapeless mass when an inspection took place, and that an inquiry into this inexplicable occurrence had been opened at the time. I did not know whether this inquiry had led to any result. I therefore at once examined the new case of tin decay at the spot, and I ascertained that, while a certain number of blocks had completely preserved their normal appearance, others had suffered a more or less profound change in their structure.

"From the very first I had inclined to the opinion that the cause of the change in structure was the exceptionally low temperature of the winter 1867-68 at St. Petersburg. (On January 26th the thermometer had gone down to −38°C.) I, therefore, in May, 1869, submitted tin to an artificially produced low temperature below the freezing-point of mercury, and I had the satisfaction to observe that tin, at this low temperature, soon underwent a change in structure entirely corresponding to that found in February, 1868. Inquiries made meanwhile had moreover acquainted me with various additional circumstances. Thus another firm informed me that another portion of Banca-tin had suffered in the same way during the winter 1867-68, and that this decay of tin at extreme cold was well known in its establishment, especially to the men employed in the tin stores; they had, indeed, a special name for this tin, a Russian word, which might be translated *tin that can be scattered about*. The Chief of a Moscow drug-house, whom I met here, told me that he had himself seen the decay of Banca-tin several times during the very cold weather in the winter fair at Irbit; the tin would swell and develop warts and drops which would adhere to a copper wire, as if they consisted of mercury; this he considered an incontestable proof that Banca-tin contained mercury.

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[6] *J. prakt. Chem. N. F.*, **52**, 428 (1851).

[7] *Mémoires de l' Académie de St. Petersbourg*, VII Series, **5**, (1870). Further references are given in *Zeit. physik. Chem.* **30**, 601 (1899).

"After this historical introduction I pass to a description of the special condition in which I found the altered tin. Whilst, as I stated already, some blocks had remained entirely unchanged, others had undergone a more or less radical alteration. These latter blocks had assumed a brittle consistency. Isolated spots at the surface with warty swellings were at once recognizable, or swellings extended from larger portions of the surface which still retained some cohesion, more or less deeply into the interior. Other blocks had lost their metallic lustre completely; they either looked dull, of a radial-fibrous texture, throughout their mass, or the surface had alone turned crystalline, whilst the interior had retained its metallic appearance; a saw cut displayed these differences at once. The completely changed blocks had partly turned into a grainy, powdered mass, like sand; other portions formed lumps of various dimensions up to the size of a fist, of loose cohesion and fibrous texture. In the specimens which had been exposed to artificial cold, the effect of the cold had apparently started from certain spots and had spread under development of a warty extumescence and of a coarse fibrous texture. Where two such centres met, fissures formed along the boundary, suggesting a rough structure; the material could easily be separated at these fissures.

"The colour of this modified tin is decidedly grey, and distinctly different from that of the ordinary bright metal. When the tin is heated this colour undergoes a very striking change. When hot water is poured over the tin, the dark grey colour becomes much lighter, almost like that of ordinary tin. It is immaterial whether dry or wet heat is applied, and neither the water nor the aqueous vapour takes any part in this change of colour. When a stoppered glass bottle, filled with sandy, dark grey tin, was heated in a water-bath until the colour had become much lighter, I noticed a not inconsiderable diminution of the volume. I then exposed such fairly white tin, of smaller volume than the grey tin from which it was obtained, again to a temperature below the freezing-point of mercury, with the curious result that the colour became dark again, and that the sandy mass which had loosely filled the bottle would not run out when the bottle was turned upside down. The volume had probably increased again, so that the grains pressed against one another and were impeded in their gliding over each other.

"When the grey tin is heated up to melting, a certain, not insignificant portion of it remains behind in the oxidized state; this again is a consequence of its broken-up structure. The fused tin regains on cooling entirely the appearance of ordinary tin, and when re-exposed to low temperature it undergoes the same changes as before, provided it had not been contaminated with other metals during fusion."

We will not stop to consider the varying opinions expressed by chemists[8] all over the world in an attempt to account for this phenomenon. However, let me stress the fact that my friend C. van Eyk and I, in a joint investigation on the subject, have verified in every detail the results described by Fritzsche.

The pictures on the screen show, (Fig. 4) a block of the normal Banca-tin, and (Fig. 5) the same block which had been returned from Moscow to Rotterdam because fraud had been suspected by the authorities. The blocks had been sent via rail from Rotterdam to Moscow and upon reaching their destination were found to be partially disintegrated into a grey powder. Analysis of the material showed only 0.05 per cent. impurities present.

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[8] Literature: *Zeit. physik. Chem.*, **30**, 601 (1899); **33**, 57; **35**, 588 (1900); **36**, 513 (1901); **48**, 243 (1904); **50**, 225 (1904); **63**, 625 (1908).

Fig. 4

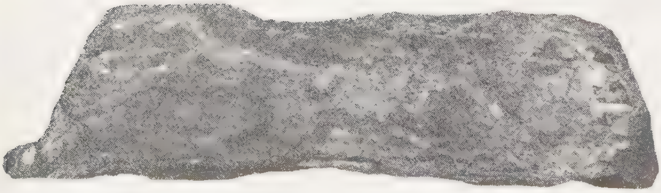

Fig. 5

SECOND LECTURE

OUR subsequent investigations into the nature of this remarkable change in tin have shown that it is to be considered a clear case of enantiotropy, as it has been demonstrated that white and grey tin may change reversibly into each other, and that there exists a transition temperature above which the one form (white tin) and below which the other form (grey tin) represents the stable modification. Before going into details concerning the determination of this transition temperature, we will perform an experiment which will enable the audience to observe that the change from white into grey tin is, as Fritzsche had previously found, accompanied by a decided increase in volume. For this purpose grey tin is introduced into the bulb *A* of the apparatus *ABKTU*, Fig. 6. Distilled water is then poured through the funnel *T* until it begins to flow from the U-tube *U* at *F*. A certain quantity of mercury is brought into the U-tube through F and its heighth is so regulated by means of the stopcock *K* that the iron weight *F* rests on the surface of the mercury. The thread

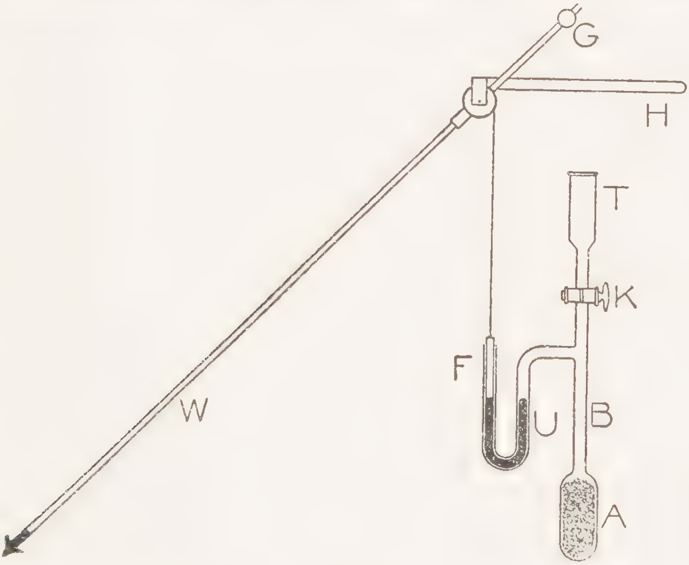

Fig. 6

to which the float is attached is of such a length that the pointer W, made of very thin wood, rests at the zero point of a divided scale (not shown in the figure). The weight *G* may be shifted, if necessary, so that the pointer may be started at any desired position. If the container *A* be surrounded by hot water, the grey tin will change into the white form. Consequently, the mercury in *F* will fall, the float will follow it downwards, and the pointer *W* will rise.

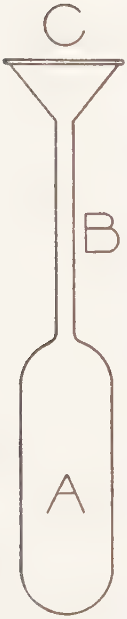

Fig. 7

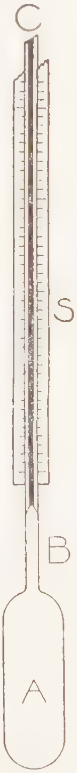

Fig. 8

For the exact determination of the transition temperature the dilatometer, Fig. 7, is employed. By means of the funnel *C* that portion of the apparatus marked A is filled with approximately equal amounts of grey and white tin. The glass tube is cut off at *B* and the capillary *S*, Fig. 8, fused on. The pipette *ABC*, Fig. 9, is then connected at *A* with the capillary *S* after some neutral solvent, *id est*, one which does not react with tin (such as petroleum), has been introduced into part *B* of the pipette. *C* is attached to an air pump and all the air is removed from the apparatus, whereupon the pipette *ABC* is turned on its axis in such a manner that the petroleum enters the tubes *A* and *S*. If the air pump is then detached the mineral oil flows through the capillary S, Fig. 8, into part *A* of the dilatometer and fills it. A very finely drawn-out capillary is then introduced into *S* and some of the mineral oil is withdrawn until the level of the liquid stands at the middle of the scale.

The dilatometer prepared according to these directions is placed in a thermostat at, let us say, 10°C. The contents of the apparatus is permitted to assume the temperature of the bath. After a certain period of time has elapsed, the position of the meniscus in the capillary is read, and observations are made in order to determine how the level of the liquid changes with respect to time. The level of the meniscus will be seen to rise, despite the fact that the temperature remains constant. Evidently white tin must be changing into grey tin at this temperature for it has been shown that this transformation is always accompanied by an increase in volume. The fact that some of that modification which is being formed, is already present accelerates the change (Compare page 25).

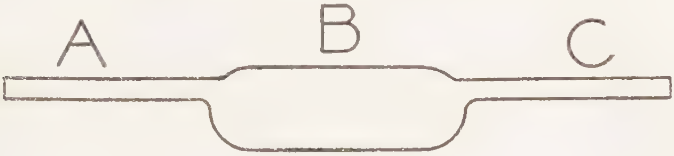

Fig. 9

The temperature of the thermostat is raised to 20°, kept constant, and the same procedure repeated. The meniscus will be seen to fall after a time. From this we may conclude that a change from grey to white tin is taking place, as this transformation is accompanied by a decrease in volume. By changing the temperature of the thermostat for each new trial, that temperature will eventually be found at which the meniscus does not change. This will be the desired transition point, *id est*, that temperature at which both forms of tin will be in stable equilibrium with each other. For tin, it is 18°C.

The following equation may be constructed:

$$\text{grey tin} \overset{+\ 18^\circ\text{C.}}{\rightleftarrows} \text{white tin}$$

Further investigations[9] have yielded results which may adequately be represented by means of a *p-t* diagram, Fig. 10. *abcd* and *fgh* are the vapor pressure curves of white and grey tin, respectively. The two curves intersect in the point *P* which corresponds to the transition point, + 18°C.

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[9] See footnote, page 28.

If the tin be cooled below 18°C. it very often happens that immediate transformation into the form stable at these temperatures does *not* take place. The white tin remains as a metastable modification and its vapor pressures at varying temperatures are indicated by the points *h*′, g′ and *f*′. The stubborness of this apparent retardation is ample explanation for the fact that the existence of a form stable below +18° namely, grey tin, was not recognized until very recently. Since most tin utensils are quite usable below 18°C. we can truthfully say that all the tin in the world is in a metastable condition, except on very warm days. Tin which is subjected to temperatures below 18°C. tends to change to the stable form. The speed with which this transformation takes place may be very slow, but eventually, perhaps after years or centuries, the complete decay of the particular article is brought about.

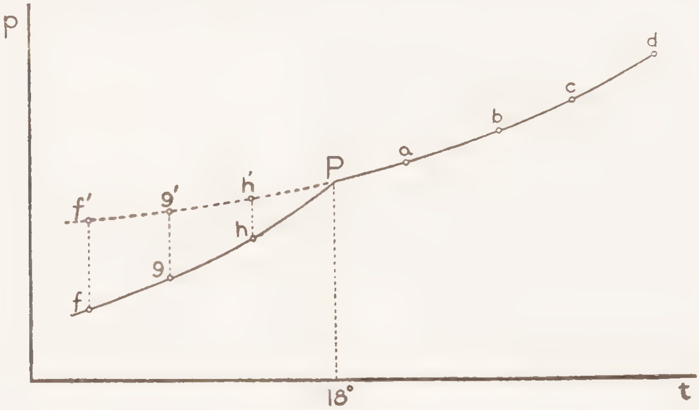

FIG. 10

This fits in very well with the observation that antiques which have been preserved in museums where the temperature is usually below 18°C., eventually change to grey tin and crumble to pieces. Fig. 11 and Fig. 12, a coffee pot and a medal dating back to 1692, very clearly show this decayed state.

In regard to the speed with which the change from white tin to the grey modification takes place, the following statements can be made. We can *a priori* give two tem-

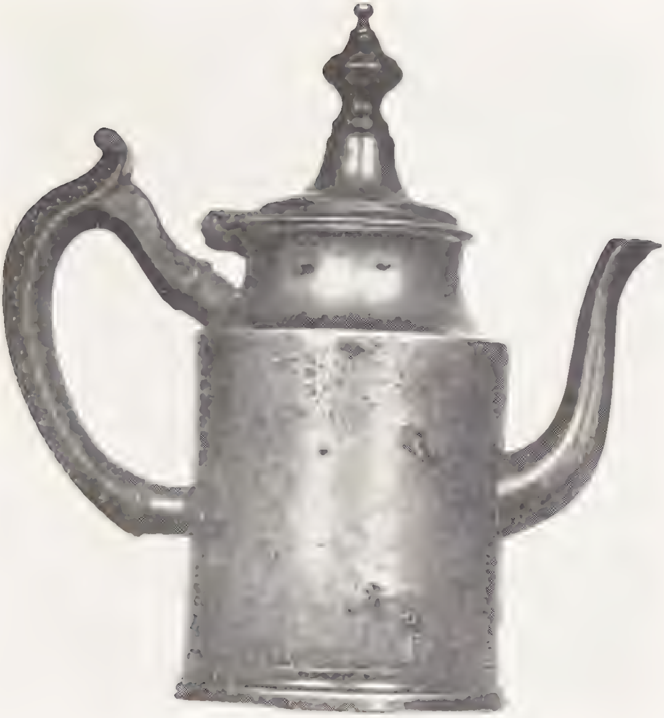

FIG. 11

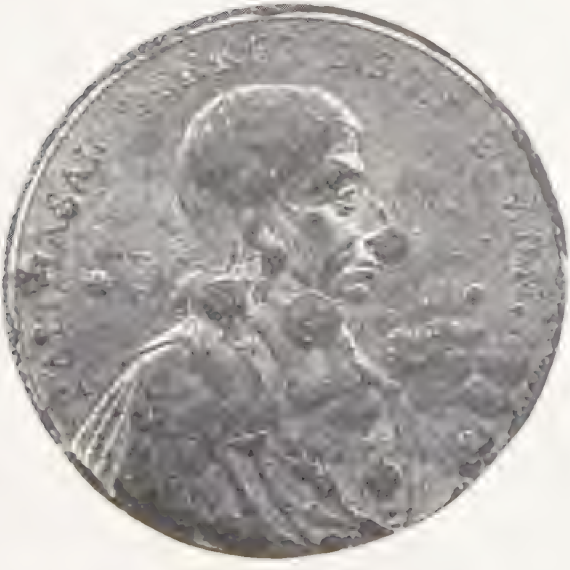

FIG. 12

peratures at which the transformation velocity is zero. One of them is the transition point where both forms may co-exist in stable equilibrium. The second is the absolute zero (−273.09), since we assume that at this temperature all molecular motion will have ceased. Since we know, as experience has taught us, that the change does take place between these two temperatures, we may conclude that the transformation velocity passes through a maximum. In fact, experiment indicates that such a maximum actually exists, and that the change from white to grey tin takes place most rapidly at −45°C., Fig. 13. Thus for the preparation of larger quantities of grey tin from the white form, the following method is to be recommended.

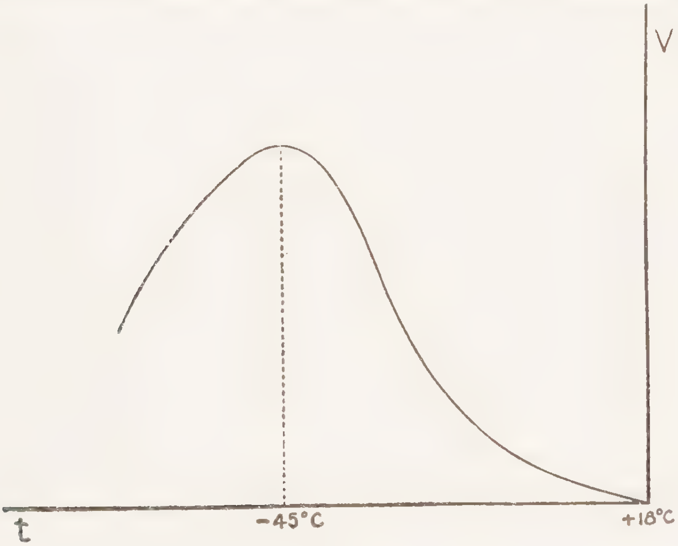

FIG. 13

Filings of white tin are brought into contact with some of the powdered grey form, as well as an electrolyte and the whole mass cooled down to −45°C. in say, liquid ammonia. In this connection it might be mentioned that the change takes place much more rapidly if the material has undergone this transformation before. It has previously been pointed out that the change from white tin into the grey modification is hastened by contact with "germs" of the latter, these have an infectious action. Since this infection has led in certain cases to an undesired disintegration of the metal, the appearance of the phenomenon has been given the name "tin disease".

But germs of the stable form are not the only factors in increasing the speed of this and similar transformations. In many cases the change is favored greatly by contact with solutions of various electrolytes, or even water. Use was made of this fact in order to bring about the above described transformation in as short a period as possible, so that it could be studied within a reasonable length of time. Even solvents for the particular modifications of polymorphic substances expedite matters. Opportunity will be given later to discuss examples of this kind. Fig. 14 shows the condition of a block of tin three weeks after its inoculation by means of a solution of a tin salt, and Fig. 15 shows the same specimen after it had been allowed to lie in the dry state for over eight years.

It is perfectly evident that the appearance of the tin disease is a very disturbing occurrence in many of the industries. A number of such cases are described in the references cited above.

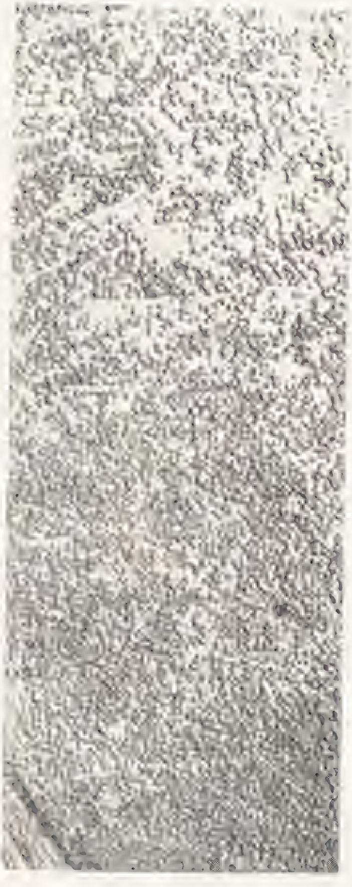

FIG. 14

FIG. 15

THIRD LECTURE

WE WILL now consider the second class of polymorphic substances, which, to distinguish them from enantiotropic materials, have been designated as *monotropic*. To gain a clear conception of monotropy let us consider a definite substance which displays the characteristics of substances of this type. Such a substance is the so-called "explosive antimony" which was discovered in 1855 by the English chemist George Gore.

If a concentrated solution of antimony trichloride in hydrochloric acid be subjected to electrolysis, using an anode of ordinary antimony and a cathode consisting of a platinum wire, there is deposited upon the latter a substance having a metallic appearance and a brilliant luster. If the electrolysis be permitted to proceed for a long enough period of time the deposit will grow in size and assume the appearance of a metallic rod. Fig. 16 shows the apparatus used for this purpose.

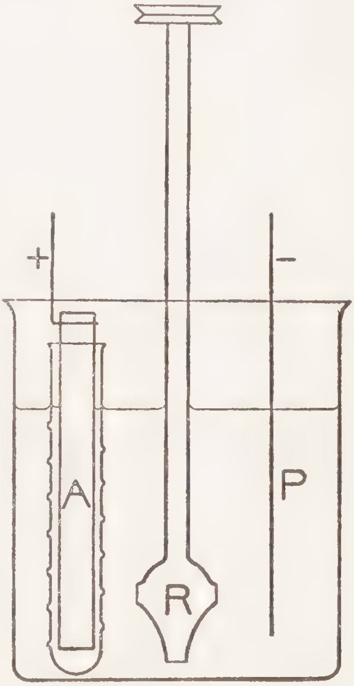

Fig. 16

The solution is contained in a beaker of about one liter capacity. *R* represents a glass Witt stirrer which is driven by a motor. *A* is a rod of antimony which is enclosed in a glass tube with small holes in it, or in a linen bag. The purpose of wrapping is to prevent the antimony from breaking off and falling into the solution. *P* is a platinum wire. The metal which is deposited on *P* during the course of the electrolysis possesses a most remarkable property. If scratched or struck it becomes very warm. This heating effect is accompanied by the evolution of white vapors of antimony trichloride. The metal itself is reduced to dust in an explosive manner. Without going into any details concerning these remarkable phenomena let me give you the conclusions which have been drawn as the result of an investigation carried out in conjunction with my friends Ringer, Collins and Strengers[10].

Antimony may exist in two different modifications which we may designate by the names α and β antimony. The relationships between these two forms may be represented most conveniently by means of a *p-t* diagram, Fig. 17. The curves *abcd* and *a′ b′ c′ d′* refer to the vapor pressures of the α and β modifications, respectively. However, the point of intersection of these two curves *P*, where the vapor pressures of the two modifications would be equal, corresponding to the transition point *P* of enantiotropic substances, (see Fig. 10) cannot be attained. Before it is reached both modifications melt, the β form at the temperature T_β (corresponding to the point S_β) and the α form at the temperature T_α (corresponding to the point S_α), these points, S_β and S_α, appearing on the vapor pressure curve

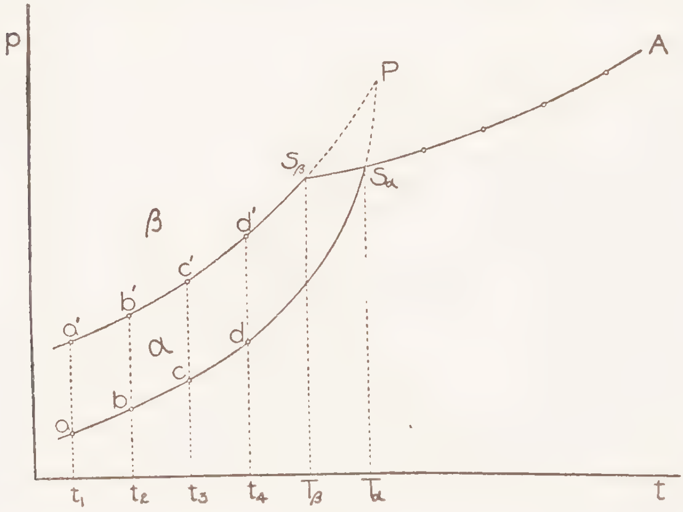

FIG. 17

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[10] Zeit. physik. Chem., 47, 1 (1904); 50, 291 (1904); 53, 129 (1905).

S_β S_α A, of the molten antimony. Your attention is called to the fact that the melting point S_β is lower than S_α.

Furthermore, the graph shows that at *all* temperatures the vapor pressure of the β modification is higher than that of the α form at the same temperature; that is, the β form always strives to change into the α modification. Therefore, the β modification may be considered as metastable with respect to the α form. In contrast to enantiotropic substances, we may designate, following Otto Lehman, as *monotropic* such solids as exhibit characteristics similar to those of antimony. They are substances which possess one form which is stable at all temperatures between absolute zero and its melting point, and one or more other forms which are less stable and which strive to change to the stable form at *all* temperatures. You will recall that the enantiotropic modifications of a substance are such as undergo reversible transformation into each other at a definite temperature termed the transition point.

Whereas the transition of an enantiotropic modification presents a reversible procedure, the transformation of a monotropic form into the corresponding stable form may be considered as irreversible. Electrolysis of an antimony solution produces the monotropic, metastable, β modification of the metal. Experiment has demonstrated that a small amount of antimony trichloride is held in solid solution with it. β antimony tends to change to the stable α form at all temperatures. If a rod of β antimony be left by itself at room temperatures the change takes place, but so slowly that it may be months or years before the transformation of the metastable modification into the stable α form has proceeded quantitatively in that direction. However, if such a rod of β antimony be scratched or struck, the local heating which results will be sufficient to increase greatly the speed of change. This local stabilization which is accompanied by a decided evolution of heat (heat of stabilization or heat of transition) serves to raise the temperature of the neighboring parts and the result is an increase in the speed of transformation. Experiment has shown that the transformation of 1 gr. of β antimony is accompanied by an evolution of 20 gram calories.

The transformation spreads quickly, so that such a rod of β antimony is converted immediately and completely into the stable metal. The violent disintegration of the metal, often explosive in character, may be explained as follows:—As has been pointed out previously, the explosive antimony produced by electrolysis always contains a certain percentage of antimony trichloride in solid solution. Since the change from β into α antimony takes place with the development of 20 gr. calories per gram, and since the specific heat of the metal is about 0.05, calculations show that spontaneous stabilization causes a rise in temperature of $20/0.05 = 400°C$. Actually no such rise in temperature is ever obtained, because part of the heat is lost by radiation and conduction. Since the boiling point of antimony trichloride is approximately 225°, it is evident that a part of the $SbCl_3$ will be expelled in a gaseous condition, and this sudden development of vapor will cause the metal to be comminuted and dispersed into small fragments. A very pretty experiment may be performed to show that the stabilization of β antimony is actually accompanied by a strong development of heat. I have here a thermometer whose bulb has been covered electrolytically with a thick layer of explosive antimony. This was done as follows:—The bulb of the thermometer is coated with a suspension of graphite in an alcoholic shellac solution and allowed to dry. This is then copper plated in the usual way. Prepared in this manner the thermometer is introduced as cathode into a solution of antimony trichloride in hydrochloric acid and the solution is electrolyzed as has been described above. After a thick enough layer of explosive antimony has been formed upon the bulb of the thermometer, it is washed with hydrochloric acid, water, alcohol, and ether. It is then enveloped in ordinary cotton and the scale of the thermometer thrown upon a screen by means of a projection lantern. If the surface of the bulb be scratched with a knife the transformation takes place and the mercury will be seen to rise to a fairly high temperature, about 300°C.

The behavior of explosive antimony gives us a clear conception of the close relation between the stabilization velocity and the temperature. An experiment will serve to bring this fact to your attention. A rod of explosive antimony is prepared and immersed in liquid air contained in a mortar. As soon as the metal has assumed the temperature of the refrigerant, it is broken up into small pieces. At the existing low temperature the rate of change is so small that the transformation into the stable form does not take place, despite the fact that the metal has been subjected to strong blows and impact. That such is the case can be demonstrated by allowing the triturated material to come back to room temperatures. If it is then struck a blow, the transformation takes place immediately, recognizable by the strong calorification. I have emphasized this fact, because it is this characteristic which has made it possible to investigate explosive antimony. In many of the experiments which were performed to obtain data concerning this substance it was necessary to secure the metal in a finely divided state before the investigation could proceed.

A survey of the known data concerning antimony will bring out the fact that as in the case of tin, even although the metastable form tends to change only very slowly to the stable form at ordinary temperatures, the change nevertheless does take place. Thus, any specimen of white tin below 18°, or of explosive antimony, will always be found to contain some of the stable form. How much of it is present cannot be deduced in advance. Since the speed of stabilization is dependent upon the temperature, the percentage of the stable form present in such a sample will depend upon its previous thermal history. Opportunity will be afforded later to make a more detailed study of this point and to discuss the influences and results of this fact.

FOURTH LECTURE

WE WILL next concern ourselves with the answer to the question:—By what methods are we able to determine whether a polymorphic substance is to be considered as enantiotropic or classified among the monotropic ones? The answer can easily be deduced from the facts with which we have become acquainted in the preceding lectures.

If it can be proved that a polymorphic substance shows a transition temperature, that is, that there exists a range of temperatures in which one modification is stable and another series of temperatures at which another form is stable, then we have a clear case of enantiotropy.

It is more difficult to show that a substance is monotropic. In order to be classified as such it must be demonstrated that there is one form which is stable at all temperatures between absolute zero and its melting point and another form (or forms) which is (are) always metastable.

We have at our disposal several methods by which we may determine the transition temperature of enantiotropic substances. One of these, in which we have made use of the dilatometer, has already been discussed.* You will recall that this method is based upon the fact that the specific volumes of the two forms of tin for instance are quite different. The specific gravity of grey tin is only 5.8 whereas that of white tin is 7.3. Thus, a change from the former into the latter will be accompanied by a diminution in volume of approximately 25%. In similar cases the dilatometer can be used in another manner for this purpose, but we shall not discuss it at this time. The whole matter is greatly simplified where the various enantiotropic modifications show a difference in color, as in the case of grey and white tin. If grey tin be introduced into a glass tube and held at constant temperatures for fairly long periods of time, a temperature may be determined at which its color does not change, and a second temperature at which it does. If these temperatures be chosen very near to each other we may (practically) assume that the first temperature is the transition point.

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* See page 29.

Careful consideration of *p-t* diagrams, Fig. 10, suggests a number of other methods which may be employed for the purpose of determining the transition temperature. For instance, if the vapor pressure of a polymorphic substance at various temperatures be ascertained, the point *P*, the intersection of the two vapor pressure curves, will represent the transition temperature *T*.

In quite an analogous manner the solubility curve of a substance may be used for the same purpose. In such cases the solubilities are plotted as the ordinates, Fig. 10, the temperatures as the abscissae. The point of intersection *P* of these curves will again give the desired transition temperature *T*.

Likewise, the study of any property of the saturated solutions at their saturation temperatures may be used to determine the transition temperature of a polymorphic substance. Thus, if the densities of saturated solutions be determined, curves will be obtained like those in Fig. 10, which will give the required temperature. The temperature at which β rhombic ammonium nitrate changes to α rhombic form was ascertained in this way[11]. However, the results obtained by these investigators are incorrect, probably because of the fact that the solutions which they employed in their determinations were not fully saturated. Further experimental work along these lines is desirable. This is also true of those cases where the transition temperature was determined by measuring the viscosity of the saturated solutions. If the viscosities of the saturated solutions of a polymorphic substance at various temperatures be made the ordinates, and the temperatures be plotted as the abscissae, the transition temperature may readily be determined by this method. Experiments in this direction were carried out by Dunstan and Langston[12], who used for this purpose a specially constructed viscosimeter. They took the time of efflux as the unit of viscosity.

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[11] Wolf Müller und Kaufmann, Zeit. physik. Chem., **42**, 497 (1903).

[12] J. Chem. Soc., London, **101**, 418 (1912).

However, this value is not a true measure of the viscosity. The viscosity is the product of the time of efflux and the density of the solution at the corresponding temperature. The microscopic[13] and thermal[14] methods may also be employed for the determination of the transition temperatures. Only two electrical methods, all of which yield exact quantitative data, will here be discussed in any detail. The transition temperature of tin, for instance, may be determined in this way. For this purpose white tin is introduced into the *H* tube, Fig. 18, at *A*, and the grey modification at *B*. The apparatus is then filled with a solution of stannous chloride to which has been added a few drops of hydrochloric acid to prevent the solution from becoming turbid. Platinum wires connect the tin in *A* and *B* with a potentiometer by means of which the electromotive force of the resulting galvanic cell may be measured. This "transition cell"[15] is immersed in a thermostat whose temperature is held at, let us say, 10°C. A definite electromotive force will be indicated by the cell at that tem-

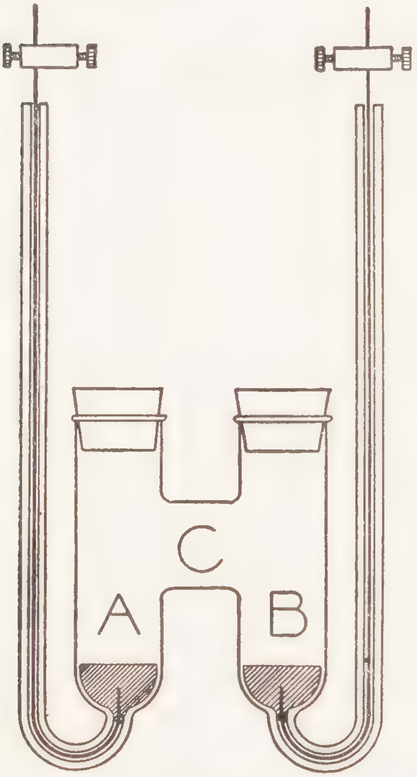

Fig. 18

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[13] See Otto Lehmann, Die Kristallanalyse, Leipzig, 1891, p. 23 ff.

[14] See Bakhuis Roozeboom. Die Heterogenen Gleichgewichte vom Standpunkte der Phasenlehre, Braunschweig 1901, **1** (1) 112.

[15] Concerning transition cells and their theory, see Ernst Cohen, Zeit. physik. Chem., **14**, 53 (1894); Ernst Cohen and Georg Bredig, ibid, **14**, 535 (1894); J. H. van't Hoff, Ernst Cohen and Georg Bredig, ibid, **16**, 453 (1895), Ernst Cohen, ibid, **25**, 300 (1898), **30**, 623 (1899), **31**, 164 (1899), **34**, 179 (1900); Ernst Cohen, Katsuji Inouye and C. Euwen, ibid, **75**, 1 (1910), Ernst Cohen and Katsuji Inouye, ibid, **75**, 219 (1910).

perature. Both forms of tin act like entirely different substances, they have their own electrolytic solution tension, the metastable white form having the higher solution tension at 10°C. Thus *A* is the negative pole, the metal going into solution at that temperature.

If the temperature of the thermostat be raised to 17 C. a different electromotive force will be indicated. Above the transition temperature the grey tin will change to the white form. This change takes place very quickly due to the presence of an electrolyte. It will soon become apparent that the change has actually taken place, since the electromotive force of the cell will have become zero. This is to be expected now that *A* and *B* have become identical. If the electromotive force of the transition cell be plotted according to the Cartesian co-ordinate system as a function of the temperature, the ordinates representing the electromotive force and the abscissae the temperature, Fig. 19, the point of intersection *T* as calculated from the *E-t* diagram will make possible an accurate determination of the transition temperature. This will be found to be 18°C.* Cadmium may be used as an example to illustrate the second electrical method which we shall discuss. This example will emphasize the fact that extreme precautions must be observed under certain circumstances, so that no

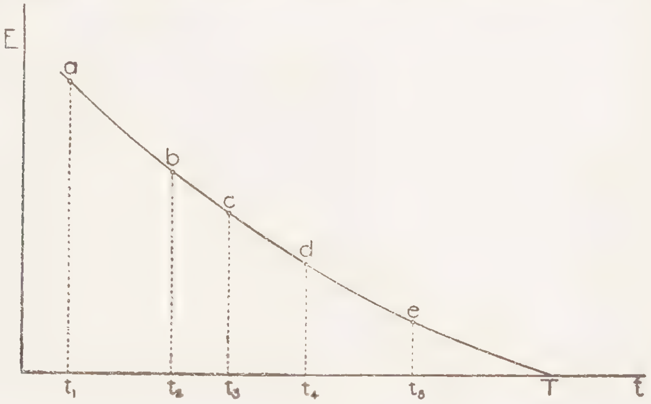

Fig. 19

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* See page 32.

false conclusions will be drawn from the experimental data at hand. It may be mentioned beforehand that dilatometric determinations have revealed the fact that cadmium may exist in at least three different forms[16]. For the time being, these may be designated as the α, β and γ forms. The relationship between the α and β forms may be brought out by the equation.

$$\alpha - \text{Cadmium} \overset{64°\text{C.}}{\rightleftarrows} \beta - \text{Cadmium}$$

These modifications form when molten cadmium is quickly cooled to a low temperature. The γ form can be prepared by the electrolysis of an aqueous cadmium sulphate solution at room temperatures. This form is, as we shall see presently, metastable under ordinary conditions. It might be mentioned in this connection that the electrolysis of solutions of certain substances often causes the formation of the metastable modification. Thus electrolysis of solutions of stannous salts below 18°C. gives the metastable white tin, and the same is true for the monotropic, explosive antimony.

In order to study the various modifications of cadmium in greater detail, the galvanic cell described by Hulett[17] as a "low-voltage standard cell" was employed as the transition cell. It is made up according to the scheme:

Cd	cadmium sulphate solution of any desired concentration	Cd amalgam 8% by weight

This cell registers electromotive force of 0.0505 volts at 25°C. and can be reproduced to within 0.0005 volt. Fig. 20 depicts such a cell. Into the bottom of a glass tube 5 cm. in height and 1 cm. in diameter there is fused a thin platinum wire, which is rolled on the inside into the form of a spiral. Another platinum wire is fused in 2 or 3 cm. above the first, and like it is rolled into a spiral. About 1 cc. of cadmium amalgam, eight per cent by weight, is introduced into the tube. Over it is poured a cadmium sulphate solution of no specified concentration. The upper platinum spiral is then covered with at least eighteen milligrams of cadmium which has been deposited upon it preferably by electrolytic methods. To do this, the cell is connected in a circuit with an accumulator, a milliammeter, and a variable resistance. About one or two milliamperes are required to deposit two to four milligrams of cadmium per hour. After the desired quantity of cadmium has been plated on the spiral the open end of tube is closed or fused together and the cell is ready for use.

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[16] Ernst Cohen and W. D. Helderman, Zeit. physik. Chem., 87, 409 (1914). See also J. A. C. S., 40, 1149 (1918).

[17] Trans. Americ. Electrochem. Soc. 7, 353 (1905).

A large number of these cells was studied and results were obtained which were subsequently verified by Frederick H. Getman[18]. These may briefly be summarized. Whereas all cells indicate an electromotive force of 0.05047 volts at 25°C. immediately after their preparation, twenty per cent. of them change in time in such a manner that the final value is only forty-seven millivolts. Seventy per cent. change so that eventually they yield only forty-eight millivolts, while only ten per cent. of the cells retain the original value of fifty millivolts. In the latter cases these observations may be interpreted to mean that the electrolysis of a cadmium sulphate solution has caused the formation of the metastable γ form. In the course of time the γ cadmium changes in about seventy per cent. of the cells to the less stable β form, giving the forty-eight millivolts (β) cells. Twenty per cent. of the cells change completely to the stable form giving the forty-seven millivolts of α cells. On the basis of this explanation, it will become evident that the three cells will show different temperature coefficients. Thus:

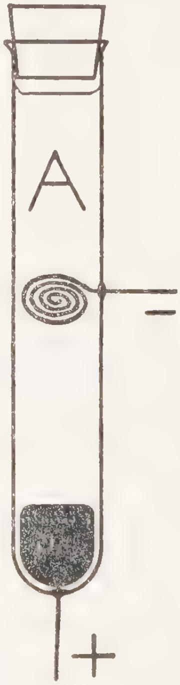

FIG. 20

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[18] J. A. C. S., 39, 1806 (1917).

For the α cells: $(E_t)\alpha = 0.04742 - 0.000200\ (t-25)$ volt (1)
For the β cells: $(E_t)\beta = 0.04862 - 0.000201\ (t-25)$ volt (2)
For the γ cells: $(E_t)\gamma = 0.05047 - 0.0002437(t-25)$ volt (3)

These results are represented diagramatically in Fig. 22, in which the ordinates represent the electromotive force, and the abscissae the temperatures. The point of intersection of the curves will give the temperatures at which one form changes into the other[19]. The calculated value thus obtained is not very exact, due to a number of reasons. First of all, the cells are reproducable only to within 0.5 millivolt. Secondly, the temperature formulas were obtained as the result of readings over a comparatively small temperature interval. The transition temperature was found to be 68.3°C. which is in fairly close agreement with the result previously determined for the change Cadmium $\alpha \rightleftarrows$ Cadmium β, namely 64°. It might be mentioned that Bridgman[20] has very recently isolated a new form of cadmium, one which is capable of existence only at very high temperatures and pressures. The relationship of this new modification to the α, β, and γ forms has not yet been studied.

As I have previously told you, Getman obtained the same temperature curves for the various cells. Concerning the behavior of the cells above 40°C. he says:

"On raising the temperature of the cells above 40°C., the temperature coefficients were found to undergo a reversal of sign. The values of the e.m.f. given by the different cells when maintained for a short time at a temperature above 40° were found to be quite divergent. On prolonged standing at this temperature, however, the divergence in e.m.f. was found to disappear and final equilibrium values agreeing within the limits of experimental error were obtained. It was found that the stabilization between 40° and 80°C. would be brought about more quickly by maintaining the cells at a temperature of 95°C.

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[19] Ernst Cohen and W. D. Helderman, Zeit. physik. Chem. 89, 493 (1915).
[20] Proc. Amer. Acad. Arts and Sciences, 60, 305 (1925).

for several days. From the data obtained with five cells which had been stabilized in this manner an interpolation formula

$$E = 0.04280 + 0.000170\,(t - 25) \qquad (4)$$

was derived by the method of least squares. On applying this formula to the data obtained with other cells, satisfactory agreement between the observed and calculated values of e.m.f. was secured.''

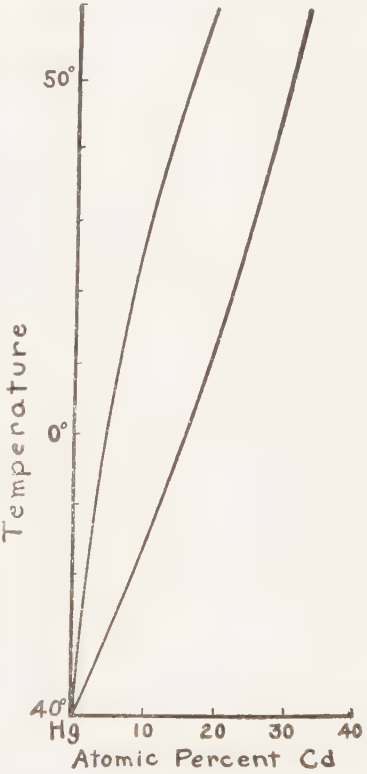

Fig. 21

After having rightly pointed out that this discontinuity in the above mentioned curves cannot be ascribed to any abrupt change in the behavior of the half-saturated solution of cadmium sulphate, Getman continues as follows:

''That the discontinuity cannot be ascribed to any change in the amalgam has been proven by the investigations of Bijl[21], in which the e.m.f. of a cell formed by connecting an 8% cadmium amalgam with a standard electrode was found to *decrease regularly* as the temperature was raised from 25° to 75°.''

Consequently he ascribes this discontinuity to the transformation of Cd α into Cd β in the vicinity of 40°, calculating the transition temperature t by means of the equation:

$$0.04742 - 0.000200\,(t-25) = 0.04280 + 0.000170\,(t-25)$$

This he finds to be 37.49°C., that is, whereas Cohen and Helderman found that Cd α changes into Cd β in the vicinity of 64°C., Getman considers 37.49°C. to be the transition temperature.

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[21] Zeit. physik. Chem., 41, 641 (1902).

In the first place I should like to call your attention to an error in that part of Getman's statement which is given above in italics. The *contrary* has been proved quantitatively by Bijl. This is evident from that part of Bijl's diagram, Fig. 21, which describes the behavior of the 8% amalgam used by Getman in his cells. This amalgam contains 13.4 atomic per cent. of cadmium and the diagram shows that the amalgam passes in the vicinity of 40°C. from the *heterogeneous* into the *homogeneous* liquid phase. For this reason, cells with a constant negative electrode which contains below 40° the heterogeneous 8% amalgam will show at this temperature an *abrupt* change of their temperature coefficient[22]. These facts were overlooked by Getman. Consequently the temperature value found by him does not correspond to the transition temperature of Cd α into Cd β. Let me recall several facts to your minds in order to prove my assertion. Getman studied several β cells between 0° and 35°. The β cadmium in these cells was prepared by maintaining at 20°C. some cadmium which had been electrolytically deposited on a platinum spiral. Getman's measurements for these β cells show that formula (2), p. 46 holds very well for temperatures between 0° and 35°. On the other hand, Getman investigated similar cells above 40°C., but in these instances the β cadmium had been prepared by holding α or γ cells at a temperature of 95°C. for several days, the cadmium being in direct contact with a solution of cadmium sulphate. Getman's measurements demonstrate that formula (4) holds good for these cells above 40°. Whereas the elements contained the *heterogeneous amalgam* as long as the temperature was kept below 40°, they contained the *homogeneous liquid* phase above this temperature. The temperature at which the e.m.f. of these two types of cells become identical corresponds to the temperature at which the heterogeneous phase of the 8% amalgam changes into the *homogeneous liquid* state. If Getman's results are accurate, the point of intersection S_2 of the curves *B* and *D*, Fig. 22, should be found at the temperature indicated by Bijl's diagram, viz. 40°.

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[22] Ernst Cohen and H. R. Kruyt, Z. physik. Chem., **72**, 84 (1910).

From Getman's equations

$$0.04862 + 0.000200\,(t-25) = 0.004280 + 0.000170\,(t-25)$$

the calculated value for *t* is found to be 40.70 which is in perfect agreement with Bijl's results.

It might be well to stop and consider the meaning of the temperature, 37.49°, thought by Getman to represent the transition temperature of Cd α into Cd β. It will be seen that the curves *A* and *D* intersect at 37.49°, viz.; this is the temperature at which the cells

Cdα	Solution of Cd SO_4	Cd amalgam 8% by weight (*heterogeneous*)
and Cdβ	Solution of Cd SO_4	Cd amalgam 8% by weight (*homogeneous liquid*)

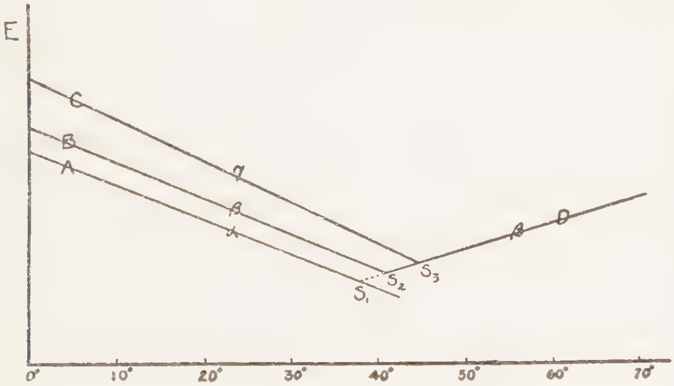

Fig. 22

have the same electromotive force. It will become apparent from Fig. 22 that this temperature must be lower than that, 40.7°, at which the *heterogeneous* amalgam changes into the *homogeneous* liquid state. As a matter of fact Getman found it to be 3° lower. This temperature does not correspond to the transition temperature at which Cd α changes into Cd β. The same may be said with regard to the point of intersection S_3 of the curves *C* and *D*. From Fig. 22 it will be seen to be higher than 40.7°. Getman actually found it to be 43.5°.

FIFTH LECTURE

ALTHOUGH the number of recognized polymorphic substances[23] among the elements and compounds is large, polymorphism has only very recently been generally accepted as a common property of matter. My investigations convince me that without exaggeration it may be said that every solid substance may exist in two or more modifications. If handbooks of inorganic and organic chemistry be cursorily examined, almost every page will contain indications of polymorphism, and almost daily within the last few years have examples of this phenomenon been brought to light. As I have already emphasized in my first lecture, it is my purpose to tell you systematically what external conditions, temperature, pressure, solvent, etc., cause the formation of modifications of the same substance and what consequences their existence will have. Before taking up these points in detail it might be well to consider further the retardation which may take place in the transformation of polymorphic substances, a peculiarity which, as we shall see presently, plays such an important role in the behavior of these substances. If white tin, Fig. 10, be cooled down below its transition temperature, that is, below 18°C., it will be found to change but very slowly to the form stable at lower temperatures, namely grey tin. Indeed, special means, such as the addition of germs of grey tin or of an electrolyte, must be employed so that the change can take place quickly enough to be noticeable. It is entirely possible that a sample of white tin which has been kept below 18°C. may be only partially changed to the stable form. This we have noticed in the discussion of the transformation of organ pipes, articles from museums, etc. Such a specimen represents a mixture of the two modifications in unknown proportions.

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[23] The table compiled by Arzruni in 1898 contains 250 examples of polymorphism. See Graham Otto's Lehrbuch der Chemie, Vol. III, p. 35, Braunschweig, 1898. With respect to organic compounds, see F. Schoenbeck, Contributions to the Knowledge of Polymorphic Substances. Dissertation, Marburg, 1901. K. Schaeling, Dissertation, Marburg, 1910.

The same is true in the case of monotropic substances like explosive antimony. Here the change takes place, even at ordinary temperatures, much more quickly than it does with tin. For this reason a sample of so-called explosive antimony may be thought of as a metastable mixture of both modifications, one in which the stable form may constitute a fairly large percentage. In general it may be said that the composition of such a mixture is a function of its previous thermal history, since the speed of transformation of the metastable form into the stable one is dependent upon the temperatures to which such an object has been exposed. If the substance exists in modifications which differ in color, as in the case of grey and white tin, a close examination of any particular preparation will immediately reveal the fact that it is not *physically homogeneous.* However, in the case of antimony which displays no such difference in color, special investigations are required to show the presence of a mixture.

These considerations make it apparent that in the future it will be necessary for us to see to it that a substance is not only *chemically pure*, but also *physically pure.* Special methods will be required to determine if a chemically pure material is composed of a single modification or whether it contains a number of them simultaneously.

The very fact that polymorphism, as you will learn, is of such widespread occurrence makes this observation of utmost importance, particularly since a study of the physical and physico-chemical properties of a chemically pure substance has for its purpose the determination of the constants of a homogeneous substance, and not of a mixture of its modifications in unknown proportions. In my further expositions I shall give you ample proof that many of the hitherto recognized physical or physico-chemical constants of solid substances are values which refer very often, if not always, to metastable mixtures which contain two or more modifications of that substance in unknown proportions. Naturally, no definite importance can be assigned to such constants. This leads us to the problem of determining methods whereby the chemically and physically pure stable and metastable modifications may be prepared and their physical and physico-chemical properties ascertained.

Two methods have actually been worked out for the preparation of the metastable modifications of tin and antimony, namely, solidification of the melt and electrolysis. Although we shall later discuss these procedures in more detail, I wish to remind you of the fact that solidification of molten tin at temperatures below 18°C. might have been expected to yield the grey form. On the contrary, the metastable white modification* resulted. In the case of antimony we might have expected the formation of the stable form by electrolysis, whereas the metastable, explosive antimony made its appearance. Likewise the electrolysis of cadmium salts yields a metastable modification.** We shall later learn that this phenomenon is quite common.

Since the investigations had shown that tin, antimony, cadmium, copper, silver, etc., were metastable structures containing several modifications, the question was raised whether or not such was the case among other elements and chemical compounds. Pointed these observations in the case of the metals at characteristic properties of the individual substances, or did they refer to special cases of a generally occurring natural phenomenon? Let us turn to the non-metals. Every page of Reichers[24] investigation concerning the allotropy of sulphur points to the fact that the behavior of this substance is not at all unlike that which we have learned to recognize in the transformation of metals. You will recall that rhombic sulphur changes reversibly to the monoclinic modification at 95°C.

$$S_{rh} \overset{95°C.}{\rightleftarrows} S_{mon}$$

Just as solutions of various electrolytes increase greatly the speed of stabilization of metals, just so do certain solvents act upon sulphur. Very small quantities have a decided influence in this direction. Quoting from the work of Reicher mentioned above, "If sulphur, recrystallized from carbon disulphide and not treated by special means to remove traces of the solvent, be melted, the solidified monoclinic substance will be found to change very quickly to the rhombic form; after a second fusion, during which a part of the carbon disulphide volatilized, the transformation took place more slowly; after a third melting still more slowly."

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* A third modification of tin, which has been recognized, will not be considered here.

** See page 45.

[24] Dissertation, Amsterdam, 1883. See also Ruys, Rec. Trav. Chim. Pays-Bas, 3, 1 (1884).

As you know, it is quite difficult to prepare absolutely pure crystalline substances by crystallization from their respective solutions, due to the fact that some of the solvent is often occluded within the individual crystals. This fact is familiar to everyone who has been forced to work with such substances. Special reference should be made to the investigations conducted by Retgers[25] and Th. W. Richards[26]. The first says, "If crystals of various salts are examined under the microscope, one is astounded at their impurity. Only very rarely is a compact and homogeneous crystal encountered; practically all of them are contaminated by inclusions of the mother liquor."

If a mixture of polymorphic modifications has crystallized from solution, the presence of such occlusions may soon lead to stabilization, *id est*, the metastable forms may disappear due to the accelerating effect of traces of electrolytes or solvents. If these occlusions are entirely removed as in the above mentioned case of the carbon disulphide in the sulphur, the stabilization velocity will be considerably decreased, that is, the resultant chemically pure substance will be a mixture of various modifications and will be *physically impure*. Further examples of this sort will be brought to our attention later. I might add that the geologist Charles St. Claire Deville[27] demonstrated that the stabilization of sulphur was not complete even after many years. He writes, "Voilà quel est le mouvement observé dans les densités (dt°, 4°) pendant cette transformation:

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[25] Zeit. physik. Chem., **3**, 289 (1889).

[26] J. Phys. chem., **6**, 92 (1908) p. 127.

[27] Compt. rend., Paris, **25**, 857 (1847).

26 avril 1845	1.9578 aussitôt après la fusion
26 avril	2.0022 trois heures après
27 avril	2.0055
28 avril	2.0131
29 avril	2.0192
1 er mai	2.0307
3 mai	2.0348
3 mai 1846	2.0453
9 juin	2.0440
4 décembre 1847	2.0498

"On voit que depuis dix-huit mois, l'accroissement de densité s'il a lieu, se fait bien lentement. Un soufre cristallisé à chaud en 1839, et qui m'a été remis par M.M. Favre et Silbermann, ne présentait, en janvier 1847, qu'une densité de 2.0508."

I have observed that the density of the pure octahedral sulphur, stable at ordinary temperatures, is about 2.07. A more exact value cannot be obtained at present since our fund of knowledge concerning this substance is rather limited. At any rate, these facts show that it has been recognized for seventy-five years that sulphur which has been cooled without any special precautions always forms a metastable mixture of a number of modifications.[28]

Those metals which have been investigated by us show a behavior very similar to that of sulphur from which the solvent has been removed. A joint investigation carried out by my friend Dr. Bruins and myself[29] has proved that occlusions are not present after melting. Experiment has demonstrated that in the cooling or chilling of the melt the modifications so formed remain in a metastable condition. The chemically pure product so obtained is thus a metastable mixture of various modifications of the specified metal; it is physically impure. In regard to chemical compounds, in addition to what has already been said, it may be shown both qualitatively and quantitatively that we daily work with substances which, though they be chemically pure, are nevertheless physically contaminated with metastable modifications.

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[28] R. Brauns, Neues Jahrbuch Min. Beil. **13**, 39 (1900); Centralblatt f. Min. 1902. p. 7; 1905, p. 678; 1921, p. 225.

[29] Zeit. physik. Chem. **94**, 443 (1920).

That retardation effects play an important role in the transformation of respective modifications can be strikingly demonstrated by the example of thallous picrate[30]. This substance which was first investigated by W. O. Rabe and more exhaustively by my friend Dr. A. L. Th. Moesveld[31] with myself, exists in two modifications, a red and a yellow, which bear an enantiotropic relationship to each other. The most recent determination of the transition temperature, carried out in my laboratory by Mr. Snijder, show it to be at 44°C. Below 44° the red modification is the stable form; above this temperature, the yellow. If the salt be prepared by interaction of aqueous solutions of thallous hydroxide and picric acid, the yellow modification precipitates, independent of temperature conditions. If the temperature of the supernatant liquid above the precipitate falls below 44°C., red crystals appear along with the yellow ones. But even if both forms are permitted to remain in contact with each other and with the solvent, stabilization of the yellow form takes place so slowly that both forms may still be present after several months. In none of the examples studied thus far has the retardation of transformation been so marked. Since both forms are differently colored their presence can be detected megascopically. If they were not colored, we should probably suppose the substances to be chemically and physically pure. The determination of the physical and physico-chemical properties would under such conditions lead to erroneous results. Uncolored substances will later be discussed where such has actually been the case.

This lagging of metastable modification towards stabilization is even more pronounced in the case of the dry substance, as a number of experiments with thallous picrate will demonstrate. Furthermore, these show that we may pass far beyond the transition temperature in going from the red to the yellow form, a rather rare occurrence.

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[30] See W. O. Rabe, Zeit. physik. Chem., **38**, 175 (1901) and S. Stevanovíc, Zeit. f. Kristallographie, **37**, 257 (1903).

[31] Zeit. physik. Chem., **94**, 450 (1920) particularly p. 458.

a) If the dry, red crystals be held for 24 hours at a temperature of 76°C., thirty-two degrees above the transition point of the compound, the material will show yellow specks in several places.

b) If the dry, red crystals be held at 100°C. for a short time, about sixty degrees above the transition point, no sign of a change will be noticeable.

c) The change takes place in a few seconds if the dry red crystals are heated to 130°C.

d) The dry modifications can be preserved for years, even when intimately mixed.

e) Traces of water, ethyl alcohol, methyl alcohol, or ether, increase the transition velocity to an enormous extent.

At present I can give you no further information concerning these phenomena. Investigations are now in progress in my laboratory in which the influence of various media, both acid and alkaline, is being studied. At any rate these show in a striking way how great the retardation of change in either direction may be. In cases where the different modifications show no change in color, grave errors may result if the substance is not tested to ascertain whether it is actually physically homogeneous and chemically pure.

In passing, it may be pointed out that the density of the red thallous picrate is 3.16 at 17° 4°; that of the yellow, 2.99 at 17°/4°.

SIXTH LECTURE

FROM among the countless examples of substances which are composed of metastable mixtures of various modifications I will choose several at random and prove to you that their physical and physico-chemical properties, insofar as they have been determined, are merely accidental values.

In the first place I would like to direct your attention toward *cadmium iodide* which was investigated with this in mind by me and my co-workers, Moesveld and Helderman[32]. On the basis of an investigation during the course of which they claimed to have prepared specimens of cadmium iodide of decidedly different densities—4.626 and 5.644—F. W. Clarke and E. A. Kebler[33] expressed the opinion that this substance was capable of existence in different modifications. Some time later J. F. Snell[34] investigated this substance and came out flat-footedly with the statement that the β-cadmium iodide of Clarke and Kebler, which was supposed to have a lower density, was nothing more than ordinary cadmium iodide contaminated with appreciable quantities of hydrogen iodide and free iodine. Despite the fact that Snell's conclusion—"a critical examination of Clarke and Kebler's work leads to the conclusion that there is no valid evidence of the existence of a form of cadmium iodide of lower specific gravity than 5.6,"—seemed perfectly logical to us, we believed it necessary to search for other modifications of the substance. In determining the direct influence of pressure upon the solubility of cadmium iodide in water we were unable at a pressure of one atmosphere to reproduce the values which Dr. C. W. G. Hetterschij[35] and I had obtained in an earlier investigation. True, the differences amounted to only a few hundredths of one per cent. at 30°C. but these differences were, nevertheless, so much greater than the usual experimental limit of error, that it was deemed sufficiently important to determine their cause.

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[32] Ernst Cohen and A. L. Th. Moesveld, Zeit. physik. Chem., **94**, 471 (1920); Ernst Cohen, W. D. Helderman and A. L. Th. Moesveld, *ibid*, **109**, 100 (1924). Ernst Cohen and A. L. Th. Moesveld, *ibid*, **94**, 482 (1920).

[33] Am. Chem. Jour., **5**, 235 (1883-1884).

[34] J. A. C. S., **29**, 1288 (1907).

[35] Zeit. physik. Chem., **94**, 210 (1920).

The cadmium iodide employed in the earlier experiments was prepared as follows. Very pure cadmium, so-called cadmium "Kahlbaum" containing only 0.005 per cent. impurity, was shaken with sublimed iodine in aqueous solution. As quickly as the solution decolorized, more iodine was added. The product was recrystallized at least twice from hot water, exposed to a preliminary drying process at 100°C., and then heated for a longer period of time at 150°, after which it was ready to be used for solubility determinations. The material used in the more recent solubility determinations was made in identically the same way, except that it was *not* heated in a practically dry condition at 100° or 150°C. Since such importance is assigned to density determinations as a criterion for the appearance of various modifications, and as this method will be employed here, it might be well to present a few facts concerning the measurement of the specific gravity of solid substances. The procedure can hardly be relegated to the category of simple manipulations, due to the fact, as we have previously pointed out on page 53, that crystals which form in solution are in most cases contaminated by occlusions of the mother liquor. Failure to take this fact into account is probably one of the reasons why exact values for the densities of solid substances are almost entirely lacking in the literature.

This difficulty can be eliminated by use of that most elegant method of Andreae's[36], which enables one to determine the density of soluble, crystallizable compounds to an accuracy of some units in the fourth decimal place. The method depends upon the fact that the crystals to be investigated are permitted to *form* within a dilatometer in such a manner that they can occlude no air within or between the individual crystals, and furthermore, that the quantity of mother liquor present can be accurately determined. Fig. 23 depicts such an apparatus. The glass bulb *C* of about 25 cc. capacity is fused to a 3 mm. glass capillary tube *B* which is ruled off in millimeter divisions. Attached to the latter is a funnel *A*. After the dry and empty apparatus has been weighed, a definite quantity of the salt is placed in *A*. If a hydrate is being dealt with, its water content must first be accurately determined. The salt, which is present both in *C* and *A*, is then completely dissolved in the solvent, for instance water, so that *C* and a part of *A* are filled with a hot concentrated solution. The

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[36] Zeit. physik. Chem., **82**, 109 (1913). See also Ernst Cohen and A. L. Th. Moesveld, *ibid*, **93**, 385 (1919) particularly page 451, Ernst Cohen and C. W. G. Hetterschij, *ibid*, **94**, 210 (1920).

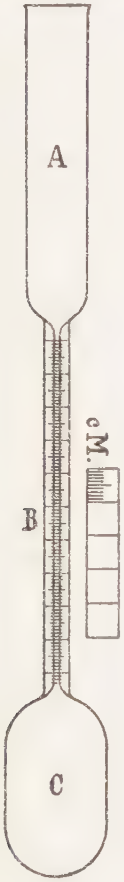

FIG. 23

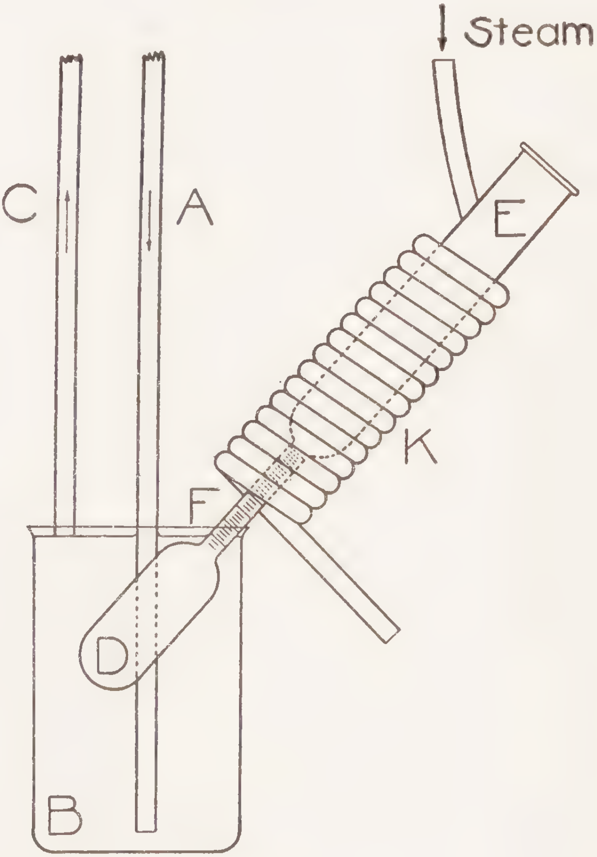

FIG. 24

apparatus is clamped in an oblique position to a stand and *A* is warmed. For this purpose the apparatus shown in Fig. 24, is used. *K* is a spiral of very fine metal tubing which is connected with a small steam boiler. The bulb *D* is placed in a beaker filled with water. The glass tube *A*, is connected with the water tap, the tube *C* is joined to a water suction pump. In this manner the level *F* of the water in *B* is kept constant. If steam from the boiler is passed through the spiral, crystals will soon separate out from the solution in *D*. The less concentrated, colder solution rises up through the tube *B*, Fig. 23, and is replaced by hotter and more concentrated solution from *E*. This movement continues as long as care is taken that by slow evaporation of water—not boiling!—the solution in *E* remains sufficiently concentrated. The apparatus can be allowed to run overnight. Eventually *D* and a part of the calibrated tube will be filled with crystals. The excess of solution in *A* and *B*, Fig. 23, is removed by means of a small pipette and these parts of the apparatus are carefully rinsed with water. The quantity of salt removed is accurately determined and subtracted from that originally introduced.

The apparatus is then placed in a thermostat and kept at constant temperature. The level of the solution in *B* is noted, from which may be calculated the total volume of the crystals and the saturated solutions, provided, of course, the volume of *C* and of the capillary *B* have been accurately calibrated beforehand. Naturally the crystals are not homogeneous, and are entirely impregnated with the mother liquor. The weight and volume of the mother liquor can easily be calculated, provided the solubility and density of the saturated solution—its specific volume—are known. The latter can readily be determined by means of the Sprengel-Ostwald-Holleman pycnometer[37].

Let m_1 = weight of the salt in dilatometer.
m_2 = weight of the salt and solvent.
d = density of salt—to be determined at the given temperature.

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[37] Rec. Trav. chim. d. Pays-Bas, **19**, 79 (1900). See also Ernst Cohen, Wilhelma A. T. de Meester and A. L. Th. Moesveld, Zeit. physik. Chem., **114**, 321 (1924) particularly p. 329.

c = concentration of saturated solution at the given temperature expressed in grams solute per gram solvent.
v_c = specific volume of the saturated solution at the given temperature.
V = volume of the bulb *C* plus the volume of that part of *B* occupied by the liquid.

Then,

$m_2 - m$ = weight of solvent added
$(m_2 - m_1)c$ = amount of solid material dissolved
$m_2 - (m_2 - m_1)c$ grs = amount of solid substance remaining in the dilatometer (1)

The weight of the saturated solution there is

$$(m_2 - m_1) + (m_2 - m_1)c = (1 + c)(m_2 - m_1) \text{ grs.}$$

and since this solution has specific volume of v_c the volume of the saturated solution in the dilatometer is

$$(1 + c)(m_2 - m_1)v_c$$

The volume of the solid substance in the dilatometer is therefore

$$V - (1 + c)(m_2 - m_1)v_c \tag{2}$$

From (1) and (2) the density of the solid substance at the given temperature may be determined*

$$d = \frac{m_1 - (m_2 - m_1)c}{V - (1+c)(m_2-m_1)v_c}$$

If great accuracy is not required, in other words, if an error of three units in the third decimal place is permissable, a pycnometer such as illustrated in Fig. 25, may be used. Care should be taken to obtain types which have necks that are as long and well ground-in as possible.

After this slight deviation from the subject matter of my lecture, I will continue my discussion of cadmium iodide. Employing the apparatus of Andreae, the density of the sample which had been dried at 100° and then at 150° was found to be 5.670 at 30°/4°. Further experiments demonstrated that the density of all samples which had been prepared by concentration of aqueous cadmium iodide solutions and subsequent drying at various temperatures for a longer or shorter period of time, was dependent to a great extent upon their previous thermal history. The density of the material was found to increase as the drying temperature rose from room temperatures to 150°C. Prolonged heating at 150° would eventually give a sample which had the limiting density of 5.670. From these observations we gathered the impression that a mixture of various modifications was obtained, one of which changed to the other in course of time. If I may be permitted to anticipate the final results in order to give you a clearer conception of what has been stated, these observations give proof of the fact that cadmium iodide exists in two forms bearing a monotropic relationship between room temperatures and its melting point, about 400°. That modification which is stable at all temperatures and whose density was found to be 5.670 at 30°/4° may be designated as α-cadmium iodide. The other which is metastable at all temperatures may be termed the β-form.

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* For sample calculations see the literature mentioned in footnote 36, page 58.

The metastable form admixed with the stable may be prepared in fairly large amounts by crystallization from certain solvents. Of these methyl alcohol yields most satisfactory results. If a methanol solution of cadmium iodide be evaporated under reduced pressure at 20°C., at which temperature the stabilization velocity of β-cadmium iodide is small, the material obtained under these conditions will be found to contain a fairly high percentage of the metastable form. In determining the density of this

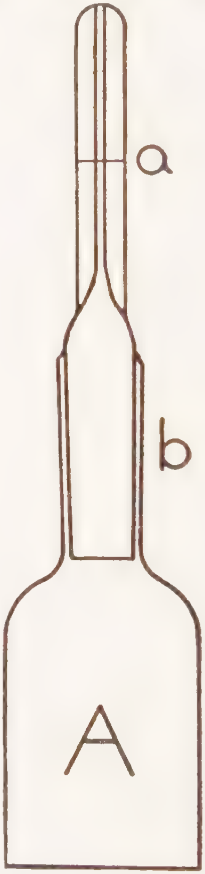

FIG. 25

product by means of a pycnometer using toluol as the confining liquid, it was found that the level of the meniscus in the capillary stem of the apparatus fell very quickly at constant temperature 30°. This seemed to indicate that stabilization took place so quickly at this temperature that an accurate density determination was well-nigh impossible. However, we did secure a value of 5.211 at 30°/4° for this preparation, quite decidedly different from that obtained for the first preparation. It is significant that toluol as well as xylol, neither of which dissolves cadmium iodide, nevertheless do increase the speed of stabilization.

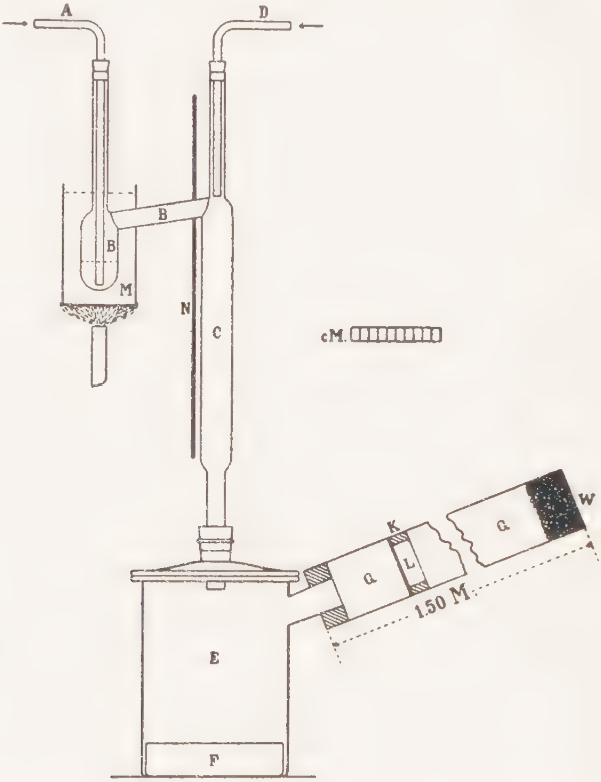

Fig. 26

If the dry material, whose density is 5.211, be heated at higher temperatures for some time, say at 100° for eighteen hours, the density of the material will increase to 5.534. If heated for some time at 150° the density will be found to increase to 5.670, the value for the stable α-modification. A perfectly anhydrous mixture of both forms, which is not in contact with any liquid, changes its density but very slowly. In view of this fact the question might well be asked: Is it possible to prepare the pure metastable β-modification in the "dry way"? This has not as yet been accomplished in the case under discussion, but since we are more concerned with a general method for the preparation of metastable forms, I will describe an apparatus by means of which we were able to obtain a sample of cadmium iodide which contained an appreciable quantity of the β-form along with the stable α-form.

The carefully dried iodide is placed in the retort *BB*, Fig. 26. *B* is surrounded by a copper container. The interstices are filled with powdered graphite. By means of a large burner the whole installation can be heated to 600°, a temperature some 200° above the melting point of cadmium iodide. The tube *C* which is fused to *BB* is protected against too high a temperature by means of an asbestos screen *N*, placed between *M* and *C*. A stream of carbon dioxide, free from oxygen, enters at *A* and is passed through the molten salt. Another current of the same gas which enters at *D* is previously cooled by passing it through a spiral that is surrounded by a mixture of solid carbon dioxide and alcohol. The purpose of this arrangement is to cool the vapor of cadmium iodide entering at *B*, which would partly or entirely condense to the metastable β-form, as quickly as possible to a temperature where the stabilization velocity is very slight.

The iodide is condensed to a solid in *C* as well as in the glass chamber *E*, at the bottom of which has been placed the crystallizing dish *F*. Because of the speed of flow of the gas a part of the salt is carried still further and collects in a finely divided form in the glass tube *GG*, 1.5 meter long. If some cotton, *W*, be placed at the end of this tube, an appreciable quantity of the salt will be found to have collected at this point at the conclusion of the experiment. Since the removal of the finely divided salt cannot be accomplished without considerable loss, there is placed in the tube *GG* a stopper *K* with a large opening *L* over which is spread some linen of fine mesh. The iodide will collect at this point and can then easily be removed.[38] Such a sample showed a density of 5.447 at 30°/4°, and it contained less of the metastable modification than that prepared from methanol solution. Obviously the temperature in *C* must still have been so high that the stabilization process took place at a fairly fast rate.

The very fact that liquids such as toluol and xylol, which are used as confining liquids in pycnometers, cause a speedy stabilization of β-cadmium iodide to take place, and thus prevent an accurate determination of the density in this manner, seems to make it desirable in investigations of this sort to have some method whereby the density may be ascertained with the exclusion of any and all liquids. We have actually employed such a method in the case of cadmium iodide, making use of the Regnault *Volumenometer*, which is described in most textbooks on physics[39]. Unfortunately the various forms of this apparatus yield rather unsatisfactory results. Since a volumenometer which would allow the accurate determination of densities even at high temperatures is to be considered an important desideratum in this field of research, I have called this point to your attention.

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[38] For particulars see Ernst Cohen and A. L. Th. Moesveld, Zeit. physik. Chem. **94**, 471 (1920) especially p. 477.

[39] See, for instance, Chwolson, Lehrbuch der Physik, 1, 331 (1902). Braunschweig, where complete references are given.

SEVENTH LECTURE

NOW if the solid substances which we handle daily are in truth metastable mixtures of the various modifications in which they may exist, it follows that their physical constants, such as their densities, are dependent upon their previous thermal history. Thus, the heat of solution* of an element or a compound is a function of the relative quantities of the α–, β–, γ . . . modifications in that substance. Furthermore, since the transformation of the metastable β–, γ– . . . modifications into the stable α–modification is always accompanied by an evolution of heat, it will become evident that those heats of solution which up to the present have been tacitly considered as the heats of solution of the stable α–modifications, will be numerically larger or smaller than those of the stable α– modifications, depending upon whether these substances exhibit a positive or negative heat of solution. That such is the case may be verified by cadmium iodide. For this reason the heats of solution (1) of the stable α–cadmium iodide and (2) of metastable mixtures were determined. Of course, it is imperative that the two samples attain the same final state so in both cases one mole of cadmium iodide was taken and conditions adjusted so that the concentration at the end bore a relationship of 1 $CdI_2 : 400H_2O$.

On the strength of what has just been said concerning the heat of stabilization, it will be seen that the heat of solution of α–cadmium iodide will be numerically greater than that of a mixture of both modifications, since the act of solution is accompanied by an absorption of heat. In carrying out these experiments Ernst Cohen, Moesveld and Helderman[40] used a specially constructed, electrical, adiabatic calorimeter which enabled them to determine the respective heats of solution to an accuracy of three parts per thousand. Fig. 27 depicts such an apparatus. The principle upon which this apparatus is based may be briefly stated[41]. If the negative heat of solution of any substance *A* in any solvent *B* is to be determined, the solvent as well as the material to be dissolved—the latter being contained in small glass bulbs which have been sealed by fusion—are introduced into a calorimeter which is entirely enclosed and is kept at constant temperature. As soon as the calorimeter, its contents and its surroundings have come to the same temperature, the glass bulbs are crushed from the outside. The temperature of the calorimeter and its contents is kept as nearly constant as

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* The term "heat of solution" as here used refers to the so-called "heat of solution in a very large quantity of solvent." The statements which are made apply to all heats of solution.

[40] Zeit. physik. Chem. **109**, 100 (1924). Ibid. **112**, 141 (1924).

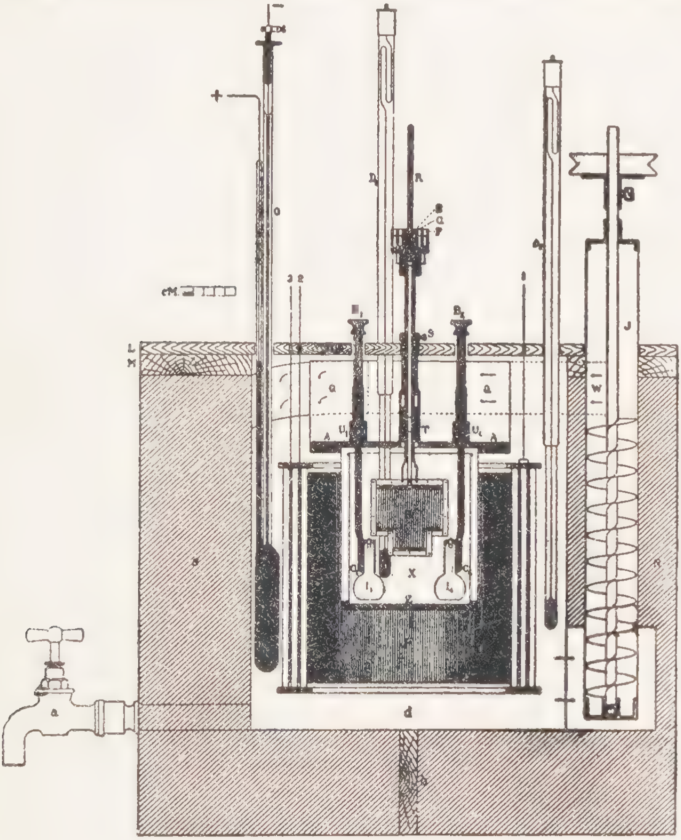

FIG. 27

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[41] S. W. Holman, Proc. Am. Acad. of Arts and Sciences, N. S. 23, 245 (1896).

possible by conveying to it the necessary quantity of electrical energy. Small unavoidable changes in temperature which do occur are taken into account and are detected by means of a thermometer which is set into the calorimeter. Except for this small change in temperature for which a correction can readily be made, the negative heat of solution is entirely compensated by the electrical energy which has been conveyed to the apparatus. By careful measurement of the electrical energy thus added, using the potentiometric set-up illustrated in Fig. 28, the desired value for the heat of solution may be obtained[42].

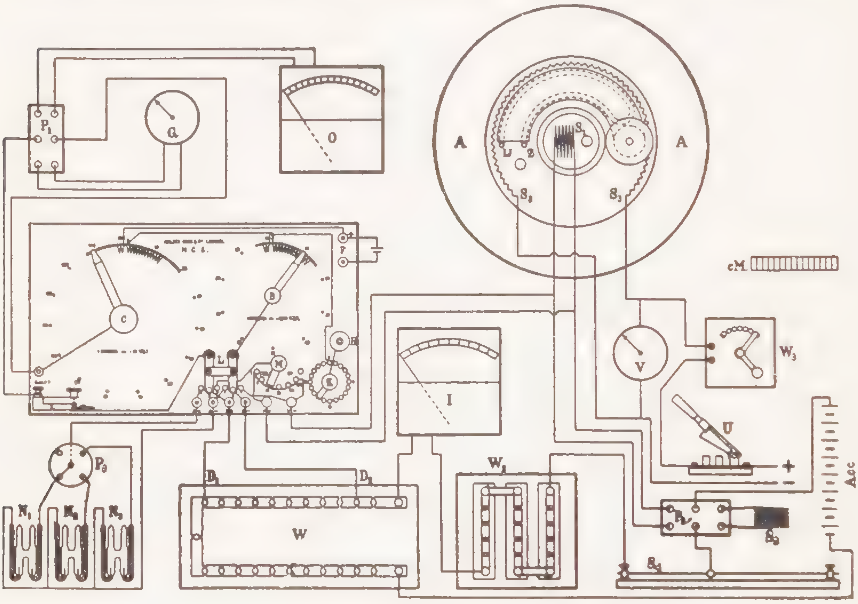

FIG. 28

In Fig. 27, *X* represents a heavily fire-gilded, copper cylinder of about 1350 cc. capacity, subsequently covered by a coating of metal lacquer (Valspar). *X* rests in the groove of a hard rubber plate that fits snugly on the copper cylinder which surrounds the calorimeter as an air jacket. This casing is fitted with a broad, flat ring upon which the brass plate *AA* lies. This slides into the copper cylinder which is soldered to the flat ring. Once the plate has been placed into position the cylinder is filled with cotton up to the wooden cover *L*. Thus *AA* is thoroughly insulated. The plate is depicted in Fig. 29 with the stirring arrangement and the attachments whereby the small bulbs containing the solute may be crushed consecutively after the calorimeter has come to a temperature equilibrium. Through the tubes U_1, U_2, U_3 and U_4, only three of which are visible in the figure, pass the brass plungers K_1, K_2, K_3, K_4 to the bottom of which are attached the small glass bulbs*. The stirrer *R* passes through the tube *T*. The paddles *H* of the stirrer, which also acts as a heater, are of such design that the stirrer may rotate freely between the glass bulbs[43]. In order to break the glass bulbs one has only to strike the knobs B_1, B_2, B_3 and B_4 with a hammer. The spiral springs automatically force the rods K_1, K_2, K_3 and K_4 back into position again. The petroleum which encompasses the air jacket is caused to circulate by a stirrer J, a modified Archimedes screw, which is rotated at 1900 r.p.m. by an electric motor. The oil flows from the space *d* through an opening in the wall of this space to the stirrer. From *W* it then takes the channel *QQ* returning

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[42] For calculations see Ernst Cohen and A. L. Th. Moesveld, Zeit. physik. Chem. 93, 385 (1919) particularly paragraph 110.

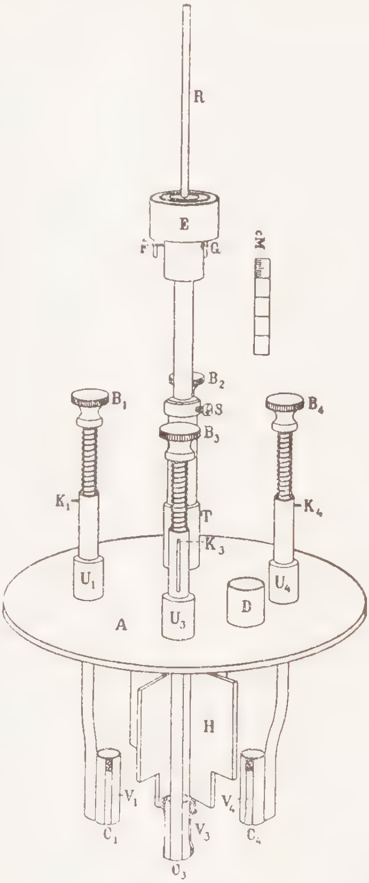

Fig. 29

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* For the construction of this apparatus see footnote 40, page 66.

[43] Concerning the details of the stirrer see Ernst Cohen and A. L. Th. Moesveld, Zeit. physik. Chem., 100, 151 (1922).

again to *d*. The temperature of the oil, and therefore also that of the air jacket, can be held constant within 0.01° by means of an electric regulator[44]. The α-cadmium iodide used for the determination of its heat of solution was prepared as follows:—Purest metallic cadmium, resublimed iodine and water are brought together in a flask and shaken until complete decoloration has taken place. The solution is then evaporated on the water bath. The resulting mixture of α- and β-cadmium iodide is kept at a temperature of 150° for several days. As soon as its density has become 5.670 at 30°/4°, that is as soon as the material has been converted entirely to the pure α-form, then and only then may it be employed for calorimetric measurements.

Metastable mixtures which still contain appreciable quantities of β-cadmium iodide are prepared by not allowing the substance obtained upon evaporation to become completely stabilized, that is, the product is heated at 150°C. for only a short time. In this way we prepared one mixture whose density was 5.302 at 30°/4°, and a second with a density of 5.596 at 30°/4°.

The results of the calorimetric measurements are given in the following table:

TABLE I

Heats of solution of the modifications of Cadmium Iodide at 18.2°C.

Wt. of solvent (water) in grams	Wt. of salt in grams	Density of the salt d(30°/4°)		Heat of solution in gr. calories		Average heat of solution in gr. calories
1099.78	55.8706	5.668	stable	−981	stable	−976
1097.32	55.7453	5.668		−971		
1098.74	55.8133	5.668		−976		
1099.62	55.8635	5.596	metastable	−951	metastable	−951
1100.00	55.8791	5.302	metastable	−929	metastable	−927
1101.07	55.9861	5.302		−922		
1100.00	55.8795	5.302		−930		

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[44] Ernst Cohen and A. L. Th. Moesveld, Zeit. physik. Chem., **93**, 385 (1919) particularly paragraph 47.

Whereas the heat of solution of the stable α-modification was found to be −976 gr. calories at 18.2°C. those of the metastable mixtures were numerically less, as we see, −951 and −927 gr. calories respectively. The greatest difference is approximately five per cent. and if the metastable β-modification is ever prepared in pure form the variance will be even greater. Only two references are to be found in the literature regarding the heat of solution of cadmium iodide. One of these determinations was made by Julius Thomsen at a temperature of 19°C. He also used a final concentration of CdI_2 : 400 H_2O. He obtained the values −943 and −981 gram calories, an average of −960 gram calories[45]. Since Thomsen makes no mention of the previous thermal history of his preparations, it cannot be said whether the difference of 4% in his results is due to the presence of varying quantities of the metastable modifications, or to other causes.

A second series of experiments was performed by H. S. Taylor and G. St. John Perrott[46], who dissolved the iodide in 0.5 *N* and 1*N* potassium iodide solutions. What has been said above is equally applicable to their results. Later, when the metastability of ammonium nitrate is taken up, we shall have occasion to consider a similar case. However, I wish to call your attention to the fact that more than half a century ago Person[47] and later Berthelot[48] observed phenomena of this sort and studied them quantitatively by calorimetric methods. These investigations seem to have escaped the knowledge of chemists and physicists in general. Person found that the heat of solution of sodium chloride was 90 gram calories less negative when the determination was made using a preparation which had previously been melted and then cooled, than if made with material which had not thus been treated. Berthelot essentially corroborated this observation, but in his specimen the difference amounted to one hundred and eighty gram calories. Not only did this later investigator find sodium chloride to act in this manner, but *all* substances which he studied with this idea in mind presented the same peculiarity. From this he concluded that salts which had previously been melted had a less negative heat of solution than those which had not been fused. Furthermore, he noted that this difference decreased in the course of time and that the heats of solution would eventually become the same if the substances were preserved at room temperatures for several months. It is a very striking fact that this difference is also decreased if the solidified salt is pulverized before the calorimetric measurement is made. This is in complete accord with our own observations.

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[45] J. prakt. Chem. (2) **16**, 328 (1877); Thermochemische Untersuchungen. Vol. III, pages 185 and 201, Leipzig 1883; Systematische Durchführung thermochemischer Untersuchungen, p. 250, Stuttgart 1906.

[46] J. A. C. S., **43**, 484 (1921).

[47] Ann. d. chim. et d. phys. (3) **33**, 452 (1851).

[48] Ibid, (5) **29**, 198, 231, 239, 295 (1883).

This following table records the results of Berthelot's experiments.

TABLE II

Substance	Difference in gram calories per equivalent of the heat of solution of the previously melted salt and that of the unfused substance.		
	After melting	After ten days	After two months
KCl	+ 170	+80	+ 20
KBr	+ 210		
KI	+ 90		
NaCl	+ 180		+ 10
$BaCl_2$	+ 30		
$SrCl_2$	+ 80		
$CaCl_2$	+ 150		
$HgCl_2$	+ 400		
$HgBr_2$	+ 300		
HgI_2	+1500		
K_2SO_4	+ 150		0
Na_2SO_4	+ 470		+260
K_2CO_3	+ 170		+ 70
Na_2CO_3	+ 350		+280

It may be mentioned that the accuracy of the results given above for the heats of solution is only 10 gram calories per equivalent. The uncertainty of the difference in the second column amounts to about 20 gram calories, but in the case of mercury salts it runs somewhat higher, about 40 gram calories.

At first Berthelot[49] made no very definite statements regarding the possible causes of this phenomena. He says: "De telles différences représentent sans doute certains états transitoires, dérivés de la constitution physique du liquide, et que l'on traduisait autrefois par le mot chaleur de fusion retenue dans l'état solide." Later he conceived a more distinct idea relative to these differences in the heats of solution. Not long after he had become acquainted with the case of mercuric iodide, he wrote, "Ce dernier écart répond à une différence d'état moléculaire tellement tranchée que les deux corps sont regardés comme isomères. Mais la même interprétation paraît applicable a tous les cas analogues."

If we examine this table more closely we will become cognizant of the astonishing fact that, since the publication of the experiments of Person and Berthelot, not less than fifty per cent. of the substances mentioned have been found to exist in a number of modifications at one atmosphere pressure—$BaCl_2$, $HgCl_2$, $HgBr_2$, K_2SO_4, Na_2SO_4 and K_2CO_3. Furthermore, it is becoming more and more evident that polymorphism is a fairly common property of solid matter. In view of what is now known in this field, it is not at all improbable that those substances noted in the table which have not yet been shown to be polymorphic, actually possess this characteristic. Investigations concerning them are now in progress in my laboratory at Utrecht. These are doubly important since neither W. Ostwald[50] or Beketow[51] were able to reproduce what Person and Berthelot observed in the case of sodium chloride.

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[49] Ann. d. chim. et d. phys. (5) **29**, 198 (1883) particularly p. 217.

[50] J. prakt. Chem., N. F. **25**, 8 (1882).

[51] Zeit. anorg. Chem., **40**, 355 (1904); see also Kurnakov, Zeit. anorg. Chem., **52**, 186 (1907).

EIGHTH LECTURE

IN MY last lecture I showed you that it has quantitatively been proved that the value which had previously been considered as correct for the heat of solution of cadmium iodide in water was an entirely accidental one; that it referred to a metastable mixture of the α and β iodides in which these two forms were present in unknown proportions. From this it is quite evident that the several physico-chemical constants of this substance need to be redetermined, using the physically and chemically pure modifications.

A glance through the literature concerning other calorific constants of elements and compounds, as, for example, the latent heat of fusion of metals, shows that the same inaccuracies exist among them as were found in the case of the latent heat of solution of cadmium iodide. Thus values have been found for the latent heat of fusion of lead[52] which vary between 5.32 and 6.45 gram calories per gram of metal. The difference is even greater with sodium where the figures run from 17.75 to 31.7. It is not at all improbable that these enormous errors may be due to other causes besides the use of metastable mixtures, but apart from this fact, it may definitely be said that such values have lost their significance because no data on the previous thermal history of the substance are given. From among the innumerable examples of this sort let us consider the case of nickel, since the measurements of its latent heat of fusion were made not only on the very purest materials, but by extremely accurate methods. As you all know two measurements are necessary to determine this constant. First of all the molten metal is dropped into a calorimeter and then, secondly, a like quantity of the metal which has previously been heated to a temperature lying near but below the melting point is dropped in. The constant can then be calculated from the difference of the total heat of the molten metal and that of the solid substance corrected for the same temperature. It is to be observed here that because of the "chilling" effect, metastable modifications may easily remain existent at lower temperatures, and for that reason the value for the latent heat of fusion may be erroneous. Thus White[53] found the latent heat of fusion of nickel to have a value of 73 gram calories per gram, whereas Wüst found it to be 56 gram calories.

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[52] References are given in an article by Ernst Cohen and W. D. Helderman, Verslagen Kon. Akad. van Wetenschappen, Amsterdam, **23**, 1220 (1915); also Wüst, Meuthen and Dürrer, Forschungsarbeiten auf dem Gebiete des Ingenieurswesens, Berlin 1908, Heft 204.

Both investigators probably used materials which were not physically consistent, since nickel exhibits a transition point at 325°C.

In the field of Thermics the data in the literature on the specific heats of elements and compounds offer plenty of evidence that little or no attention has been paid to the *physical* purity of the substances which were investigated, and that a revision of these constants has become necessary.[54]

From among the many instances of this kind, I have chosen ammonium nitrate, as this substance shows in a very striking way how necessary it is to be certain not only of the chemical purity of a compound, but also of its physical purity, before it may be employed for the determination of its physico-chemical constants.

It was Frankenheim, to whom we are also indebted for many extremely interesting investigations in the field of polymorphism, who discovered in 1854 that ammonium nitrate is polymorphic[55]. Although this investigator described only two modifications, Otto Lehmann[56] was able to prove that there were at least five forms which were capable of existence at ordinary atmospheric pressure. Several years ago Bridgman[57] isolated a sixth form, stable only at very high pressures. Fig. 30 represents qualita-

[53] Papers from the Geophysical Laboratory No. 420, Chem. Met. Eng. **25**, 17 (1921).

[54] Ernst Cohen, Zeit. physik. Chem., **89**, 489, 748 (1915); Ernst Cohen and A. L. Th. Moesveld, Zeit. physik. Chem., **115**, 151 (1925).

[55] Pogg. Ann., **93**, 17 (1854).

[56] Dissertation, Strassburg 1876, Zeit. Kryst. **1**, 97 (1897), Wallerant, Bull. Soc. Franc. de Minéralogie 1905, p. 311, Compt. Rend. **142**, 217 (1906); Behn, Proc. Roy. Soc., London, A, **80**, 444 (1908).

[57] Proc. Am. Acad. Arts and Sciences, **51**, 581 (1916).

tively the *P-T* diagram of those modifications stable at ordinary pressures. The melting point of the salt is 169.6°C. However, the following transformations may take place

$$\mathrm{I} \overset{125.2^\circ}{\rightleftarrows} \mathrm{II}, \qquad \mathrm{II} \overset{84.2^\circ}{\rightleftarrows} \mathrm{III}, \qquad \mathrm{III} \overset{32.3^\circ}{\rightleftarrows} \mathrm{IV}, \qquad \mathrm{IV} \overset{-18^\circ}{\rightleftarrows} \mathrm{V}$$

These are accompanied by certain volume changes; thus

I → II—contraction
II → III—expansion
III → IV—contraction
VI → V—expansion

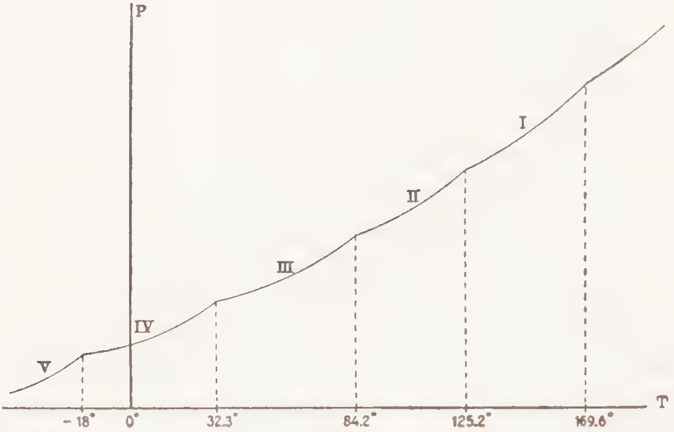

FIG. 30

The very fact that different investigators have obtained widely divergent values for the transition temperature III → IV[58], running from 31° to 36° as extreme figures, seems to indicate that a strong retardation accompanies the transformation. Besides this, Behn found that II could be undercooled from 84 to 45°C. without the change taking place, and that V, even if in contact with IV, did not change at +18°C. From his observations Bridgman concluded that "ammonium nitrate is a substance for which it is particularly difficult to force the reaction from one phase to another to run to completion." This he found true in many other instances, which is entirely in accord with our own earlier observations.

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[58] See Early and Lowry, J. chem. Soc., London, 115, 1387 (1919).

Bridgman[59] determined experimentally the values for dT/dp and ($v_{III} - v_{IV}$) occurring in the Clapeyron-Clausius equation $\frac{dT}{dp} = T\frac{v_{III} - v_{IV}}{W}$ and calculated *W*. In this equation *p* represents the pressure, *T* the absolute transition temperature of the respective modifications, v_{III} and v_{IV} their specific volumes at this temperature, and *W* the heat of transition. The following table gives his results for the transformation III ⇆ IV.

TABLE III

Pressure in Kg./cm²	Temperature in degrees C.	v_{III}—v_{IV} in cc/gm.	dT/dp
1	32.0	0.02026	0.0311
200	38.5	0.02051	0.0336
400	45.4	0.02077	0.0360
600	52.9	0.02102	0.0385
800	60.8	0.02128	0.0410

On the basis of these results it seemed evident to us, my collaborator J. Kooy and myself,[60] that the values obtained by Bridgman for ($v_{III} - v_{IV}$) were undoubtedly erroneous: because of the pronounced retardation, they were probably too low. We therefore took up the problem of determining in various ways the value for ($v_{III} - v_{IV}$) at atmospheric pressures. Bridgman obtained the value 0.02026 cc/gm (see table) by measuring the displacement of the piston of the pressure apparatus in which the transformation IV → III had taken place.

Concerning the earlier measurements of ($v_{III} - v_{IV}$), it may be remarked that Bellati and Romanese[61] obtained the value 0.01963 cc/gm. It is indeed worthy of notice that these same investigators found the density of IV at 0° to be 1.674 and believed this figure to be correct because it was the mean of the values 1.635 and 1.737 found by Joule and Playfair, and by Schröder, respectively. These widely divergent results might have suggested to them that they were working with physically impure products.

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[59] Proc. Am. Acad. Arts and Sciences, **51**, 581 (1916).

[60] Zeit. physik. **109**, 81 (1924).

[61] Att. del R. Istituto veneto, **4** (VI), 1395 (1886); Il nuovo Cimento (3), **21**, 1 (1887).

For a second determination of $(v_{III} - v_{IV})$ we are indebted to Behn. A detailed account is not given, but from his paper it may be deduced that $(v_{III} - v_{IV}) = 0.022$ cc/gm. at 32°C. On the basis of a careful dilatometric investigation the transition temperature of III $\leftrightarrows$ IV was found at my laboratory in Utrecht to be 32.3°C. The most recent work of Early and Lowry places it at 32.1°.

The value for $(v_{III} - v_{IV})$ at the transition temperature 32.3°C. was determined in two ways. By the first method the specific volumes of III and IV were measured separately using Andreae's apparatus. The other method yielded this difference by direct measurement. This may be accomplished by the following procedure. A carefully weighed quantity of the physically and chemically pure modification IV is placed in the bulb of a dilatometer*; the latter is filled with a liquid in which the salt is practically insoluble. We used toluol. The air is very completely removed by means of a vacuum pump. At the same time the apparatus is heated, care being exercised that the transition temperature is not overstepped. A capillary is fused to the bulb and behind it is placed a porcelain millimeter-scale. The dilatometer is then immersed in a thermostat which is kept at exactly 32.3°C. for several hours. If the height of the liquid does not change, if, let us say, it remains at S^1 mm., the temperature of the thermostat is raised several degrees, say 36°C. Then IV will change completely over to III within one hour. If the level of the meniscus does not change in the course of time, the temperature is lowered to 32.3°C. If there is no change even at this temperature within several hours another reading, S^2 mm. is taken. The volume of the capillary between S^1 and S^2 is then determined by filling the tube between these two points with mercury and weighing it. From the weight of mercury the volume change $(v_{III} - v_{IV})$ at the transition temperature 32.3°C. may be calculated.

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* Later I will tell you how the physical purity of polymorphic substances may be controlled.

Going about it in this way, we found for

$(v_{III}-v_{IV})$ at 32.3°C.

By the method of Andreae	By means of the Dilatometer
0.0220 cc/gm	0.0221 cc/gm

For reasons which I shall not discuss here, the second value is to be considered the more reliable. You can see that the value for $(v_{III}-v_{IV})$ at 32.3°C. found by Bridgman differs by not less than eight per cent. from that determined by Behn and ourselves, and, as we predicted, it proved to be low.

Closer scrutiny of column 3 of the Table III on page 77, reveals in an astonishing way how regularly the value for $(v_{III}-v_{IV})$ rises with increasing equal increments of pressure, but strangely enough the value for the highest pressure, 800 Kg/cm^2, does not come up to ours for one atmosphere pressure. It is our theory that in Bridgman's experiments only a portion of the ammonium nitrate took part in the transformation. This supposition is probably true in view of what Bridgman himself says. "Two series of runs were made, separated by an interval of a year. For each of these series of runs the material was hammered dry into a perforated steel shell and the pressure submitted directly to it by kerosene. For the second run, the salt was subjected to a preliminary drying in vacuum at 100°. No difference in behavior between the two runs to be attributed to this cause was to be detected. The second series, repeating the first, was made necessary by the fact that the measurements of $\triangle v = (v_{III} - v_{IV})$ given by the first series were irregular. The reason for this is that ammonium nitrate is a substance for which it is particularly difficult to force the reaction from one phase to another to run to completion." Obviously various parts of the salt mass underwent no transformation in the "first run," whereas a particular part failed to change at all pressures during the course of the "second run." The latter is not at all improbable judging from the manner in which the experimental samples were prepared. For if the salt is hammered into the steel form mentioned above, it is entirely possible that one such pellet may have changed all-together, whereas a second, despite the fact that the contact between the two left nothing to be desired, did not do so.

Experiments which I started years ago in conjunction with Dr. Moesveld and which have been continued for a long time may cast more light upon this point. If a warm, saturated solution of thallous picrate be cooled below the transition temperature of the salt—you will remember that the red form changes to the yellow at 44°C.*—both forms will crystallize out simultaneously and will remain in their respective states for several months even in contact with the solution. If the water be allowed to evaporate, a *mixture* of both modifications is obtained despite the fact that they are in intimate contact with each other. Such mixtures we have preserved for more than five years at 15°C., some 25 degrees below the transition temperature.

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[*] See page 55.

NINTH LECTURE

IN MY last lecture I called your attention to the fact that the value obtained by Bridgman for $(v_{III} - v_{IV})$ was about eight per cent. low, and for no other reason except that instead of using the physically pure modification, he made his determinations on mixtures of the two forms. That this is the case can be checked in another manner.

Bridgman calculated the heat of transformation *W* of III → IV by means of the equation

$$dT/dp = \frac{T(v_{III} - v_{IV})}{W}$$

after he had determined experimentally the values for dT/dp as well as $(v_{III} - v_{IV})$. Whereas the value for $(v_{III} - v_{IV})$ was appreciably low due to the fact that mixtures were used instead of the pure modifications, that of dT/dp is in no way influenced by this fact. On the contrary the presence of both modifications is most desirable when studying the influence of pressure upon the transition temperature, for it serves to prevent the retardation of the transition. It is evident that Bridgman's result for dT/dp is probably not in great error. Because of the fact that $(v_{III} - v_{IV})$ was incorrectly determined his value for the heat of transition *W* will be afflicted with an equally as large error—eight per cent.

Let us substitute his values in the formula.

$T = 305$; $dT/dp = 0.0311$; $(v_{III} - v_{IV}) = 0.02026$ (1 kg. cm.) = 42.66 gm. calories

$$\text{Then } W = \frac{305 \times 0.02026}{0.0311 \times 42.66} = 4.66 \text{ gm. calories/gm.}$$

In collaboration with my friend Dr. Helderman I determined the heat of transition by the calorimetric method[62]. It is true that Bellati and Romanese[63] obtained the value 5.02 gm. calories/gm., but it cannot be said with certainty that these investigators had the physically pure modifications. In fact it may be concluded from their communication on the density of the preparations which they employed that they were working with metastable mixtures. I mentioned this fact previously in connection with another topic*. Moreover, the method of procedure adopted by them in determining the heat of transformation is open to a good deal of criticism.

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[62] Ernst Cohen and W. D. Helderman, Zeit. physik. Chem., **113**, 145 (1924).

[63] Atti del R. Istituto veneto(6) 4, 1395 (1886); also Il nuovo Cimento (3) **21**, 1 (1887).

Another set of values for the heat of transformation was recorded by Mondain Monval[64] but even these were not accurate enough for our purposes as Mr. Bredée[65] and I demonstrated in a joint investigation. The experiments performed by Dr. Helderman and myself are based upon this one premise. If the heats of solution per mole of the two physically and chemically pure modifications III and IV in any suitable solvent be determined at the transition temperature, 32.3°C., at one atmosphere pressure, and if care be taken that the final concentration be the same in both cases upon complete solution, then the heat of transformation will be equal to the difference of the heats of solution of the two modifications at the transition temperature.

In connection with another investigation we determined the shape of the curves obtained when, at the transition temperature III $\rightleftarrows$ IV, the intermediate heats of solution are plotted as functions of the concentration of the corresponding aqueous ammonium nitrate solutions. If the ordinates represent the values for the intermediate heats of solution per mole, and the abscissae the concentrations of the solutions employed for the purpose, the desired value for the heat of transformation will be equal to the difference between the ordinates at any abscissae value whatsoever.

I shall speak later concerning the manner in which we were able to control the physical purity of the modifications III and IV. The intermediate heats of solution were determined in the electrical, adiabatic calorimeter which I described in one of my former lectures*. The results which were obtained are presented in the following table.

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* See page 77.

[64] C. R. Paris **177**, 175 (1923). Thesis, Paris 1924; Ann. d. chim., **3**, 72 (1925).

[65] Zeit. physik. Chem., **117**, 143 (1925).

* See page 66.

TABLE IV

Intermediate heats of solution of ammonium nitrate modifications IV and III in solutions of ammonium nitrate of different concentrations. Temp. 32.3°C. (Transition temperature.)

Name of the modification	Initial Concentration in gm. per 100 gms. solution	Final concentration in gm. per 100 gms. solution	Mean concentration in gm. per 100 gms. solution	Intermediate heat of solution in gm. calories per mole	Mean of intermediate heat of solution in gm. calories per mole (found)	Intermediate heat of solution in gm. calories per mole (calculated)	Calculated minus found
IV	12.52	15.04	13.78	−4899	*−4903*	−4902	+1
IV	12.55	15.08	13.81	−4906			
IV	12.52	14.98	13.75	−4904			
III	12.52	14.98	13.75	−4512	*−4509*	−4502	+7
III	12.52	14.98	13.75	−4505			
IV	26.53	28.47	27.50	−4123	*−4120*	−4125	−5
IV	26.53	28.47	27.50	−4116			
III	26.47	28.49	27.48	−3716	*−3717*	−3725	−8
III	26.46	28.54	27.50	−3718			
IV	40.30	42.34	41.32	−3579	*−3584*	−3577	+7
IV	40.35	42.39	41.37	−3583			
IV	40.29	42.22	41.25	−3589			
III	40.29	42.22	41.25	−3190	*−3187*	−3177	+10
III	40.28	42.22	41.25	−3183			
IV	54.07	55.47	54.77	−3200	*−3200*	−3197	+3
IV	54.07	55.47	54.77	−3199			
III	54.07	55.47	54.77	−2799	*−2796*	−2797	−1
III	54.07	55.47	54.77	−2792			
IV	68.40	69.10	68.75	−2935	*−2940*	−2945	−5
IV	68.40	69.10	68.75	−2944			
III	68.40	69.10	68.75	−2540	*−2539*	−2545	−6
III	68.40	69.10	68.75	−2538			

The experimentally measured values of the intermediate heats of solution of modification IV $(Q_i)_{IV}$ because of their dependence upon the concentration of the solution c, may be represented by the following equation which was calculated by the method of least squares:

$$(Q_i)_{IV} = -5910 + 83.057c - 0.73476c^2 + 0.00224c^3 \quad (1)$$

A similar equation represents the experimentally determined values of $(Q_i)_{III}$ for modification III.

$$(Q_i)_{III} = -5510 + 83.057c_1 - 0.73476c_1^2 + 0.00224c_1^3 \quad (2)$$

If in equation (2) c_1 be made equal to c, then the desired heat of transformation of III → IV at 32.3°C. may be calculated

$$W = (Q_i)_{III} - (Q_i)_{IV} = -5510 + 5910 = +400 \text{ gm. calories/gm.}$$

Since the molecular weight of ammonium nitrate = 80.1,

$$W = +400/80.1 = 4.99 \text{ gm. calories/gm.}$$

Our value is, as you see, some eight per cent. higher than that calculated by Bridgman for his measurements*.

Before I close I should like to comment upon other investigations which have concerned themselves with the transformation of ammonium nitrate III into IV. It is true that the value which Bellati and Romanese found, namely 5.02 gm. calories gm., varies but little from ours. But in their investigation, as has frequently been found in the published work of others, their apparently correct result was due to the accidental balancing of errors. Further examples of such mistakes will be taken up in connection with Braun's Law which will be discussed in some detail in my lectures on Piezochemistry.

The determinations of Tammann[66] and those of Lussana[67] from which the heat of transformation of ammonium nitrate III into IV may be calculated, need not be discussed here, since their measurements are hardly of sufficient accuracy to be of use for our purposes.

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*See page 81.

[66] Kristallisieren und Schmelzen, Leipzig 1903, p. 299.

[67] Il nuovo Cimento (4) 1, 97 (1895).

TENTH LECTURE

SINCE our investigations have demonstrated that the physico-chemical constants of a chemically pure substance are of importance only when that material is also physically pure and consists of only a single modification, it might be well to consider the methods whereby the physically pure substance can be prepared. In order to do this it is first of all necessary to study the conditions under which the stable and metastable forms are formed. It will soon become evident that very little is known concerning this matter and that new investigations are sorely needed. Although a detailed consideration of this problem is somewhat irrelevant to the subject matter of these lectures, the complexity of the many existing relationships will become apparent in the particular cases which I shall discuss.

Incidental to my discussion of the stable and metastable forms of cadmium iodide, I have already pointed out that evaporation of an aqueous solution of this compound always resulted in the formation of a metastable mixture of the α and β cadmium iodides. It was noticed that solutions of the iodide supersaturated to a great extent and that crystallization was abnormally delayed. A thorough investigation into this peculiarity by Dr. A. L. Th. Moesveld[67] and myself brought to light the interesting fact that solutions of cadmium iodide could not be evaporated at 100°C without the resultant formation of at least *traces* of cadmium hydroxide, a substance which retards the crystallization process because of the extent to which it is adsorbed. If a solution of cadmium iodide is concentrated to the saturation point of the stable α form, crystallization will not take place immediately. The crystal nuclei of the α modification which then form in solution are ineffective, due to the presence of traces of the hydroxide. Continued evaporation of water increases the degree of supersaturation with respect to the α form until the solution attains a concentration equivalent to a saturated solution of the β modification. At that point crystal nuclei of β cadmium iodide form in solution, but these too adsorb the hydroxide which prevents their growth. However, the solution will in the meantime have become so concentrated, due to continued evaporation, that the α and B crystal nuclei will nevertheless increase in size: thus both modifications eventually crystallize out together. Our experiments demonstrated that, even though the speed of crystallization was greatly diminished by adsorption, the crystal nuclei were not rendered entirely inactive.

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[67] Zeit. physik. Chem. 94, 450, 482 (1920).

From what I have just said it may be gathered that metastable modifications are either formed not at all, or only with utmost difficulty, when adsorption effects are not present, that is, when impurities are absent. In accord with this opinion are the observations of Johnston, Merwin and Williamson[68] who, in a very interesting article on the "Precipitation of Unstable Forms", state that the natural calcite, the stable form of calcium carbonate, usually occurs in very pure form, whereas natural aragonite, the metastable modification, contains such impurities as the carbonates of lead, strontium and zinc. This might seem to indicate that the formation of metastable modifications is somehow dependent upon the presence of impurities. The mysterious action of the so-called "Lösungsgenossen"[69], *Agents minéralisateurs*[70], or "mineralizers", may possibly fit in with this explanation. Mercuric iodide is another substance whose behavior illustrates in a very striking manner the important role played by traces of impurities in the formation of metastable forms. Although unable to determine the solubility of the metastable yellow mercuric iodide in absolutely pure alcohol at 25°, Reinders[71] did observe that the salt remained in the metastable condition when shaken for four hours with acetone which contained certain impurities.

During the course of these lectures we have become acquainted with a number of methods which lead to the formation of metastable modifications. Peculiarly enough they happen to be the very methods which are usually employed for the production of the *chemically* pure substance, namely, crystallization, chilling of the melt, sublimation, distillation, etc. That stabilization even under such conditions very often takes place may be explained by the fact that many solid substances occlude traces of the solvent during the process of formation and we have seen that such inclusions accelerate the stabilization velocity to a marked extent[72].

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[68] A. J. Sci. **16**, (4) 504 (1916).

[69] See Grundlagen de physikalisch-chemischen Petrographie, H. E. Boeke, Berlin 1915, p. 324.

[70] For compilation of literature on the subject see P. Niggli, Geol. Rundschau, 3, 472 (1912).

[71] Zeit physik. Chem., **32**, 494 (1900) particularly p. 514.

How can we tell whether or not a given chemically-pure substance is also physically pure, that is, exists in only a single modification? Up to the present time it has been extremely difficult to answer this question. More research is very necessary in order that our limited knowledge of this field may be extended. Let me indicate a possible method of attack by describing two specific cases[73].

If it is desired to prepare a sample of physically and chemically pure grey tin, one in which white tin is no longer present, it is only necessary to enclose filings of the chemically pure white modification in a glass tube and reduce the temperature to −45°C*. In order to determine whether or not any more of the white tin is present, the resulting product may be introduced into a dilatometer, using toluol as the filling liquid, and observations made from time to time of the position of the meniscus in the capillary tube when the temperature is kept constant at −45°C. The difficulty lies in the fact that a considerable length of time is required to change the last traces of the white tin to the stable grey modification, and it is even much more difficult to detect the presence of extremely small residual quantities of the white modification by the dilatometric method. If the grey tin which has been obtained in the above manner be changed back to the white form and these experiments be repeated a number of times, a procedure which causes the transformation to take place much more quickly,* density determinations will eventually indicate the fact that a limiting condition has been attained in the case of a particular product. Repetiton of this process on a number of samples of white tin is desirable.

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[72] See Ernst Cohen and A. L. Th. Moesveld, Zeit. physik. Chem., **94**, 450 (1920). Ernst Cohen and H. R. Bruins, Zeit. physik. Chem. **94**, 465 (1920).

[73] Ernst Cohen and W. D. Helderman, Zeit. physik. Chem., **113**, 145 (1924). Ernst Cohen and A. L. Th. Moesveld, ibid, **109**, 97 (1924).

* See page 33.

*See page 33.

The values for the density of the physically and chemically pure tin so obtained may conveniently be checked by X-ray method of Debye and Scherrer. As you know, the density of either modification may be calculated from such an X-ray photogram. This method is particularly applicable in the case of tin, because the use of the physically pure modification is unnecessary. Mixtures will do just as well. Naturally, the density obtained for the physically pure form by means of the pycnometer should check with that given by the X-ray method*.

The question may very well be asked whether or not the X-ray method may be employed for the qualitative detection of one modification in presence of another. Although observations in this direction are rather limited, it may in general be said that the present day technique in this field is still too crude to permit the detection of small quantities of physical impurities. Dr. N. H. Kolkmeyer is now working on this problem in my laboratory. In the case of tin, fairly large percentages of the second modification must be admixed in order that its presence may become apparent.

However, the importance of this method is very strikingly brought out in the case of silver iodide[74]. Incidental to an X-ray analysis of this substance, Wilsey found[75], using the Debye-Scherrer powder method, that it crystallized in the cubical system. This result was subsequently verified by Davey. In the meantime, doubt was cast upon the correctness of these results by Aminoff who on the basis of his experiments concluded that silver iodide belonged to the hexagonal system. In his book "Survey of existing Crystal Structure Data", Wyckoff lends more credence to the results of Aminoff, and states that his own experiments lead him to place silver iodide in the hexagonal system. Regarding the fact that others had decided to place the substance in the cubical system he says—"Silver iodide is particularly interesting because in the ease with which it was assigned a cubic structure though possessed of a hexagonal symmetry, it furnishes an excellent illustration of the insufficiency of unaided powder photographs and sounds a warning of the dangers arising from a disregard of available crystallographic information."

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* An investigation carried out in my laboratory by Dr. Douwes Dekker on tin will be published in the near future.

[74] Ernst Cohen and A. L. Th. Moesveld, Zeit. physik. Chem., **109**, 97 (1924), See also V. Kohlschütter and P. Scherrer, Helv. Chem. Acta **3**, 337 (1924).

[75] Wilsey, Phil. Mag. (6) **42**, 262 (1921); **46**, 487 (1923).

However, it has long been known that silver iodide may exist in two different modifications. The transition point at atmospheric pressure lies at 146° C.

$$\text{AgI (hexagonal)} \overset{146^\circ}{\rightleftarrows} \text{AgI (cubical)}$$

On the basis of what I have so often emphasized in these lectures, it is to be expected that a mixture of both modifications in unknown proportions will be obtained at ordinary temperatures, unless special precautions are taken in the preparation of the silver iodide. Indeed, the results obtained by Wilsey using better apparatus and materials strongly support this opinion. He says, "The conclusion is that both crystal forms exist, most of the samples showing a mixture of the two in which the hexagonal form predominates. The discrepancies in the results reported by different observers appear to be due to differences in the samples examined rather than in the methods of analysis used." He states further, "The evidence appears quite conclusive that every sample of silver iodide studied contained the cubic form. In a few cases none but the cubic structure was evident, in some one or two faint lines were present which belonged to the hexagonal form, while in most of the samples the hexagonal form predominated."

Although Wilsey undertook no systematic examination of the conditions governing the formation of one or the other modification, he did mention the fact that the first sample which was cubical was prepared by precipitation. The other cubical products were obtained by fusion of the salt and subsequent chilling in cold water. The first-mentioned hexagonal crystals formed simultaneously when either precipitation, chilling, or the slow cooling of the fused salt was used in the preparation of the salt. Silver iodide thus presents the same sort of phenomena as do other substances with which we have already become acquainted.

That the scientist must overcome tremendous obstacles in order to prepare the physically and chemically pure substances may be very well illustrated by the behavior of ammonium nitrate. You will recall that it was necessary to prepare the physically and chemically pure modifications III and IV[76] of this substance in order that the calorimetric measurements recently discussed in these lectures* might be made. Accordingly a product was chosen as the crude material for both modifications which after its recrystallization from a solution saturated with salt at 100°C., contained no appreciable impurities.

Modification III, whose range of stability lies between 32.3° and 84.2°C., was made by two methods yielding Preparations IIIA and IIIB respectively.

Preparation IIIA was prepared by separating a portion of the crude salt from its mother liquor and placing it in a drying oven, where it was kept at 75° for a period of two months. It was occasionally ground up finely in a mortar in order to expose a fresh surface and to destroy any vacuoles which might have been present. Finally it was placed in a desiccator over phosphorus pentoxide and kept in it at a temperature of 40°C. for several weeks.

In order to prove that the resulting material was actually the pure modification III its density at 32.3°C., the transition temperature, was determined. In an earlier investigation carried out in conjunction with Mr. J. Kooy this value was found to be 1.654 at 32.3° 4°, whereas that of modification IV proved to be 1.716 under similar conditions. Xylol was employed as the filling liquid for the pycnometer. Two independent determinations using two different pycnometers indicated the density of this particular product to be 1.701; a day later, using a new sample, it was found to be 1.700 at

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[76] Ernst Cohen and W. D. Helderman, Zeit. physik. Chem., 113, 145 (1924).

* See page 81.

32.3°/4°. After standing in contact with xylol for twenty-four hours its density was found to have increased to 1.705 at 32.3°/4°. It appeared very likely that the original product IIIA had consisted of pure modification III, but that a partial transformation had taken place during the course of the pycnometric measurements. On the basis of our observations on cadmium iodide it seemed very improbable that the totally dry salt would have undergone at room temperatures a partial or complete change into IV. However, it may be that in contact with the xylol in the pycnometer, after the latter has been evacuated and placed in a thermostat at 32.3°C., this change may have taken place to some extent. This supposition was subsequently verified by further experiments which were carried out on new samples of modification III, namely IIIB.

Sample IIIB was prepared by dissolving a large quantity of recrystallized ammonium nitrate in water and evaporating the solution in a drying oven at 60°C. The salt was found to be free from moisture after four days. It was then ground up and placed in a desiccator over phosphorus pentoxide at a temperature of 60°C. After four more days its density was determined. The dry salt was placed in a pycnometer, the latter was placed in a thermostat and the temperature kept constant at 32.3° for some time. As soon as the substance had assumed this temperature the pycnometer was filled with toluol which had previously been warmed up to 32.3°C. Density determinations then gave the values 1.651 and 1.653 at 32.3°/4°, proving conclusively that the pure modification III had been obtained. A large supply of this form was preserved over phosphorus pentoxide in a desiccator at 60°C. for the calorimetric measurements* to which previous reference has been made.

Finally in order to present infallible evidence that the method employed for finding the density of sample IIIA had led to partial stabilization and transformation into modification IV, two portions of IIIB were taken and their densities were measured in identically the same way as was employed for IIIA. The dry substance was weighed, placed in a pycnometer, and xylol which had not been warmed was added. The pycnometer was then placed in a thermostat at 32.3°C. The values for the density were found to be 1.693 and 1.698, indicative of the fact that such a treatment had actually caused partial stabilization.

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* See page 81.

Let us turn next to the preparation of the physically pure modification IV whose temperature range of stability lies between −16 and −32.3°C. Two batches were prepared, IVA and IVB respectively. A moist sample of ammonium nitrate was obtained by crystallization, at temperatures between 100° and 18° from a solution which had originally been saturated with the salt at 100°C. It was placed together with a beaker of water under a bell jar. After a month the water was replaced by sulphuric acid and the bell jar evacuated. The salt was ground up daily in a mortar. After two weeks phosphorus pentoxide was substituted for sulphuric acid and the drying was continued for a further six weeks. During this time the salt was pulverized every few days. Density determinations yielded the values 1.713 and 1.714 at 32.3° 4°, whereas Mr. Kooy and I had obtained the figure 1.716 as the result of an investigation in which the material was prepared in an altogether different manner.

In making up the second sample of modification IV, a quantity of ammonium nitrate which had been heated above 32.3°C. for some time was used as raw material. In order to convert the whole mass into modification IV, it was moistened with water and left standing at 18°C. After several days the salt was placed in a vacuum over sulphuric acid, then over phosphorus pentoxide. Two independent density determinations yielded the value 1.647 at 32.3°/4°.

Since our experiments with cadmium iodide[77] had shown us that the metastable form of this salt could easily be stabilized by contact with toluol which had been distilled over phosphorus pentoxide, we attempted to change ammonium nitrate III into modification IV by placing it under dry toluol at 18°C. But no stabilization took place even after several days. The toluol was then removed by washing with alcohol and ether, and the salt was allowed to remain in contact for a period of twenty-four hours with a saturated solution of ammonium nitrate at 18°C. After the material had stood in vacuo over sulphuric acid, then over phosphorus pentoxide for several days, its density, which had originally been 1.647, was again determined and was found not to have altered. Forty-eight hours of contact with an aqueous solution of ammonium nitrate caused the specific gravity to rise to 1.677, twenty-four hours more under toluol gave the values 1.680 and 1.678, seventy-two hours, still under the same solvent, 1.680 and 1.678. Thus it may be said, that *neither contact with a saturated aqueous solution, nor with toluol or xylol at 18°C. causes a complete transfomation of modification III into IV.*

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[77] Ernst Cohen and A. L. Th. Moesveld, Zeit. physik., **94**, 471, 482 (1920).

I admit that I may have somewhat overemphasized and spent too much time upon the preparation of the pure modifications of ammonium nitrate, but I did this in order to show how difficult it very often is to obtain a pure product, and how necessary it is that new investigations be made in this field so that more light may be cast upon the external conditions which govern these transformations. Even at that, it is to be noted that the phenomena which have been discussed thus far are concerned exclusively with those transformations which take place at a pressure of one atmosphere. However, the beautiful investigations recently completed by Bridgman[78] concerning polymorphism at high pressures have shown that certain modifications formed at very high temperatures and pressures are also capable of existence under ordinary conditions. For instance, he was able to change white phosphorus at 200° and 12000 atmospheres into a black form which had very decidedly different properties. Although it is recognized as an irreversible change, the stability relationships between the black phosphorus and the other forms have not yet been definitely determined. At any rate, it is quite evident that future consideration of the problems with which we have concerned ourselves here must give greater emphasis to the effects of pressure, particularly where the discussions include those substances which occur in nature as minerals.

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[78] Proc. Am. Acad. of Arts and Sciences, **51**, 55 (1915), **51**, 581 (1916), **52**, 57, 91 (1916); Physical Review, N. S., **3**, 126 (1914), **6**, 1 (1915); Proc. Am. Acad. of Arts and Sciences, **1**, 513 (1915); J. A. C. S., **36**, 1344 (1914).

Ladies and Gentlemen:—Summing up what has been said in these lectures it may be stated that most, if not all, hitherto determined physico-chemical constants of solid substances are in need of a revision, since it is very probable that the present values refer not to the physically and chemically pure modifications, but to physically impure and metastable mixtures which contain the respective forms in unknown proportions. This state of affairs opens up an immense field of research to scientists and investigators, and one which may yet have many a surprise in store for us. In the limited time at my disposal I have been able to give you only a brief outline of this interesting subject, but it is nevertheless one which presents an entirely new perspective to science. May these lectures have given you renewed faith in the correctness of the words of the poet:

"There are more things in heaven and earth, Horatio,
Than are dreamt of in our philosophy."

PART II

SOME PROBLEMS IN PIEZOCHEMISTRY

SOME PROBLEMS IN PIEZO-CHEMISTRY
ELEVENTH LECTURE

ALTHOUGH the study of the influence of temperature upon physico-chemical reactions has for many decades enjoyed a progressive development, a fact that has found expression in construction of special laboratories dealing only with high or low temperature work, exact quantitative investigations concerning the influence of high pressures, a study which we have termed piezo-chemistry, a word derived from the Greek πιέζειν meaning *to press*, have been taken up only quite recently.

It was not until engineering science was able to produce an apparatus by means of which very high pressures could be attained and also maintained constant for an indefinite period of time that it became possible to study various problems whose solution was of importance not only for pure chemistry and physics, but also for geology.

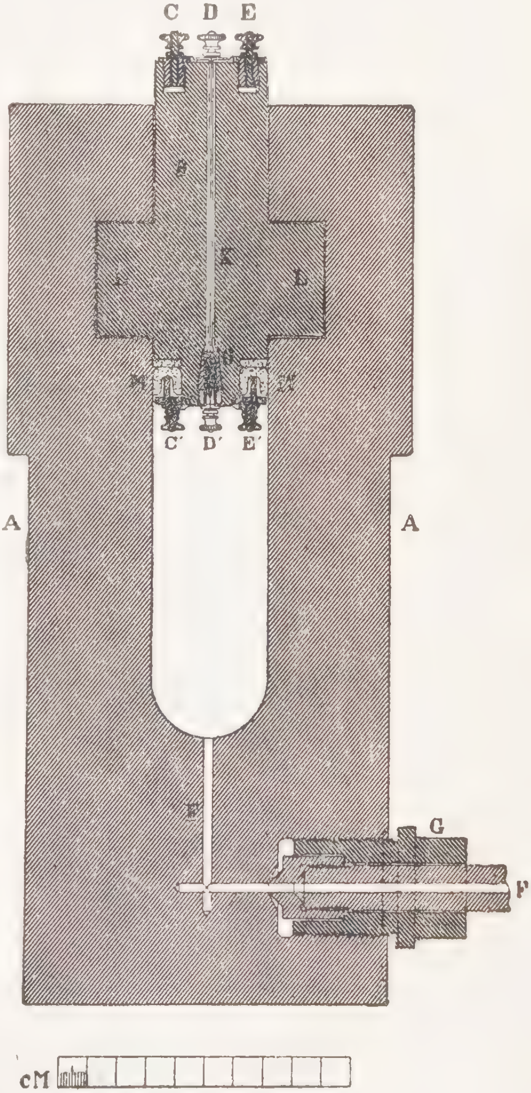

Fig. 31

In these lectures I will take up a number of such problems[79].

It might be well, first of all, to describe briefly the apparatus employed in piezo-chemical investigations in particular, as they have been developed during the past years at my laboratory at Utrecht. I shall not attempt to give you a detailed description, for this you will find in the original articles.

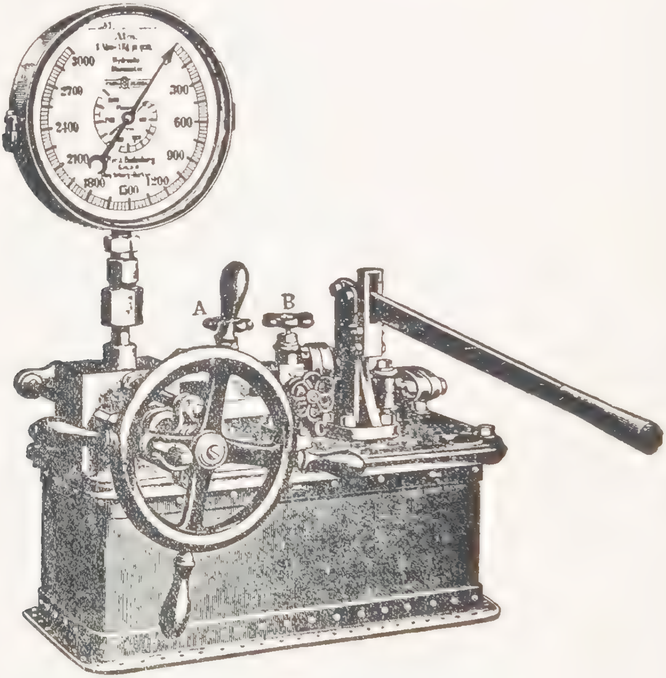

FIG. 32

The apparatus by means of which the influence of pressure upon certain phenomena may be studied is contained in a steel compression bomb AA[80], Fig. 31, filled with mineral oil or mercury, into which oil may be forced by means of a high pressure pump. When the apparatus inside the bomb is to be used for electrical measurements, the necessary wires may be connected to the outside in-

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[79] Piezochemie kondensierter Systeme by Ernst Cohen and W. Schut, Leipzig 1919, gives a summary of all of the available information up to that time on this subject.

[80] Ernst Cohen, Katsuji Inouye and C. Euwen, Zeit. physik. Chem., **75**, 257 (1910).

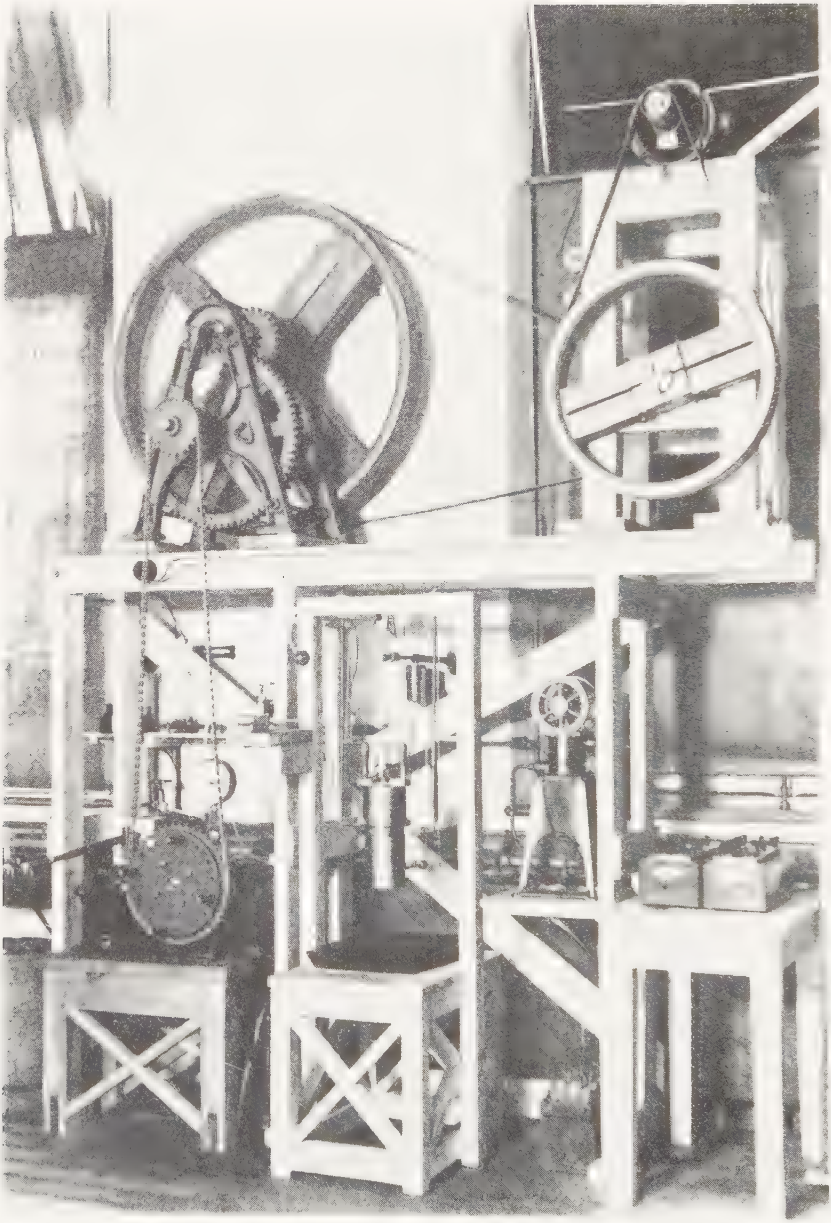

Fig. 33

struments by means of the binding posts C D E C' D' E' (a fourth is not shown in the diagram) which pass through the cover plate L K L. As it is necessary in most cases that the pressure remain constant for indefinite periods of time, the apparatus is so arranged that upon change in pressure an electric motor is shunted in automatically which puts the pump, Fig. 32, into operation. The latter then forces the oil into the bomb until the original pressure has been restored. The variations amount to about one per thousand. Fig. 33 shows the manner in which the movement of the electric motor is transmitted to the pressure mechanism of the pump. Since the ordinary spring pressure gauges change in the course of time, the pressure is checked by means of a weight pressure gauge as depicted in Fig. 34. The principle upon which it operates is very simple. A steel block, Fig. 35, is bored out in the form of two co-axial cylinders of unequal diameters. The upper cylindrical part has a surface of, for example, 3 cm^2., the lower of 2 cm^2. A piston of the same form is ground into

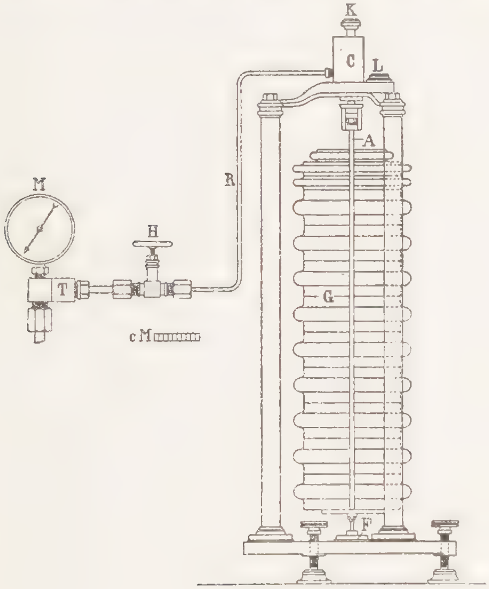

Fig. 34

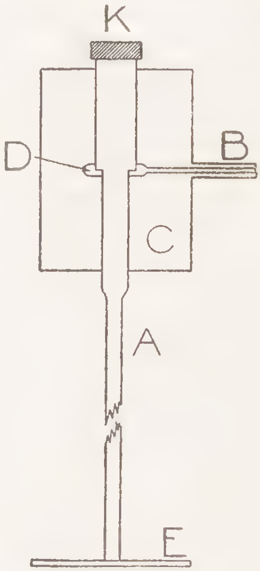

Fig. 35

this opening in such a manner that a viscous liquid like oil may be forced between it and the walls of the steel block. If then there be forced through the side channel B under the piston some liquid such as oil, say at a pressure of 1000 atmospheres, this pressure will be exerted upon a surface of one sq. cm. and the piston will be raised up with a force of 1033 kg. In order that the balance be restored a weight of 1033 kg. must be added to the piston. This is done by placing weights upon the plate E located at the bottom of the rod A. If for the present the friction of the piston in the cylinder be disregarded, it will become evident that by placing 1034 kg. on E, the balance will be destroyed. The piston will move downward until the liquid is compressed to a point where it also is under a pressure of 1034 kg. If on the other hand, the plate E be loaded with 1032 kg. the piston will rise.

Until now the frictional resistance of C has been left out of consideration. However, it is of utmost importance that errors from this source in the measurement of pressure be avoided. This may be accomplished by using as the compression liquid one which is at the same time viscous enough so that it may be forced between the piston and the wall of the cylinder. This in itself will not do away with friction, but only when the piston as well as the attached weights are put into rotation on its own axis.

The reading of the spring gauge may be checked very conveniently before and after each experiment by means of the weight pressure gauge, to which it is connected by means of a T connection, Fig. 34. While A rotates, the pressure on the spring gauge is noted. The difference in pressure between the actual reading and that equivalent to the weights yields the error of the gauge at that particular pressure.

The pressure bomb is set in a thermostat whose temperature can be kept constant by means of an electric regulator within a few thousandths of a degree. Contrivances by which the bomb may be shaken while under pressure will be discussed later.

TWELFTH LECTURE

LET US now consider some of the problems in this field. I will choose as the first for discussion the question of the *Influence of pressure upon Reaction Velocity*. The answer to this question is, in itself, of utmost importance, and moreover it will give us clearer insight into the mechanism of chemical reactions. Moreover, when sufficient data have been accumulated, it will probably be possible to answer certain questions in geology which thus far have baffled solution. The various reactions in the interior of the earth take place under enormous pressures and any conclusions regarding them are certainly premature so long as our knowledge concerning the influence of pressure upon reaction velocity is as limited as it now is[81].

After the exact quantitative experiments carried out in my laboratory in Utrecht had shown that pressure exerted a profound influence not only upon the saponification of ethyl acetate but also upon the inversion of cane sugar, and that this effect could be either positive or negative, the query arose as to whether this effect were primary or secondary. For elucidation of this question it may be said that an increase in pressure changes in a quantitative fashion several factors which have an important bearing upon reaction velocity, such as viscosity of the reacting medium, the degree of dissociation of the reacting substances, their association, etc. Since it formerly was not possible to introduce corrections for the above factors in the values obtained experimentally for the effect of pressure, the question as to whether pressure exerted a primary or secondary effect remained unsettled. To obtain answer to this question two ways are open to us. The influence of pressure upon a given reaction may first be studied, and next its effect upon the above-mentioned factors, and the results may then be introduced in our calculations. It must also be known how the reaction velocity varies with a change in these factors.

Or we may study the action of pressure upon the speed of such reactions as closely resemble one another. In such cases the corrections will be approximately equal. Any difference in the velocity of the reactions must then be due to those conditions which were not the same in the specific cases, or to the nature of the reaction itself. For instance, the influence of pressure upon two ionic reactions may be investigated in very dilute aqueous solution. Under such conditions the influence of pressure upon the viscosity and the association of the solvent will be the same, as well as changes in ion mobility and degree of dissociation, provided that similar electrolytes be employed. Thus only the specific nature of the reaction remains as a factor. If the pressure has no bearing upon the reactions as such, but is only secondary, then the effect should be quite similar in both cases.

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[81] For the earlier literature, which is principally qualitative in nature, see Ernst Cohen and W. Schut, Piezochemie kondensierter Systeme, Leipzig 1919, p. 395.

For the solution of this problem A. L. Th. Moesveld[82] studied the influence of pressure upon the reaction

$$5\ HBr + HBrO_3 = 3\ Br_2 + 3\ H_2O$$

and compared the results which he had obtained with those found for the saponification of ethyl acetate

$$CH_3COOC_2H_5 + NaOH = CH_3COONa + C_2H_5OH$$

in aqueous solution under practically identical conditions.

In both cases conditions are very much alike in that the same solvent is employed and an ionic reaction takes place in which very strongly dissociated electrolytes take part. Except for the reactions themselves the only difference between them lies in the fact that in the saponification of the ester.

$$OH' + CH_3COOC_2H_5 = CH_3COO' + C_2H_5OH$$

one ion is replaced by another, whereas the twelve ions present originally in the equation

$$5\ HBr + HBrO_3 = 3\ Br_2 + 3H_3O$$

disappear entirely leaving only non-electrolytes as the products. Because of the disappearance of the ions this reaction is accompanied by an appreciable positive volume change. The saponification reaction is likewise attended by a positive volume change,[83] but probably to a lesser degree. In the latter case this is due to the fact that sodium hydroxide is hydrated to a greater extent than the resulting sodium acetate. Thus, if the action of pressure upon reaction velocity is connected with a change in volume taking place during the reaction, then this effect should reveal a difference in magnitude, but not in sign.

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[82] Zeit. physik. Chem., 103, 486 (1923).

In the study of the influence of pressure upon reaction velocity the experimental electrical methodology employed by Ernst Cohen and H. F. G. Kaiser[84], first described by Bogojawslensky and Tammann[85] was followed. Because of its universal application in this field I shall outline it briefly, and at the same time take up with you the velocity of saponification of ethyl acetate by sodium hydroxide.

This velocity may be represented by the equation

$$k = \frac{1}{t_2 - t_1} \cdot \frac{C_1 - C_2}{C_1 C_2}, \text{ where } t_2 - t_1 \text{ gives the}$$

time during which the reaction has taken place, C_1 is the concentration of the reactants, or of the sodium hydroxide when equivalent quantities are used, at the time t_1, and C_2 the concentration at t_2. The actual procedure which was employed by us is actually nothing more than the well-known Kohlrausch method for measuring the resistance. From the latter values the concentrations of the solutions may readily be determined. This method possesses many obvious advantages. After the mixture to be investigated has been placed under pressure at constant temperature, the concentrations $C_1, C_2 \ldots$ at the times $t_1, t_2 \ldots$ may be determined by measuring the resistance from time to time using the ordinary Wheatstone bridge, alternating current and telephone. One complicating factor does enter despite the fact that very dilute solutions, 0.02 N, were employed. James Walker[86] once wrote as follows concerning this experimental procedure. "The chief conditions for the convenient application of the method are: first, that there should be a considerable difference in conductivity between the initial and final systems, and second, that the change in conductivity should be proportional to the progress of the reaction. It occurred to me that these conditions would be well fulfilled in the saponification of an ester by a caustic alkali. The conductivity of the alkali, say sodium hydroxide, is much greater than that of the sodium salt produced by the saponification owing to the high velocity of the hydroxyl ion as compared with the salt ion. Since, too, sodium hydroxide and sodium salts of mono-basic acids are approximately equally ionised under the same conditions, the ionization in dilute solutions remains practically the same throughout the saponification, and thus the alteration in the conductivity is almost exactly proportional to the progress of the reaction." It has been proved that the latter is not applicable. Therefore it has been necessary at a given temperature to determine empirically for each of the various pressures and employing known solutions the relationships between the concentration of the reactants and the electrical conductivty. If the saponification is allowed to proceed at the same temperature and under a known pressure, and if the conductivities of the reacting mixture be taken at the times t_1, t_2 . . ., the concentrations corresponding to the measured conductivities may readily be deduced from the conductivity-concentration curve for that pressure.

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[83] Benrath, Zeit. physik. Chem., **67**, 501 (1909).

[84] Zeit. physik. Chem., **89**, 338 (1915).

[85] Zeit. physik. Chem., **23**, 13 (1897).

[86] Proc. Roy. Soc. London, **78**, A 157 (1906).

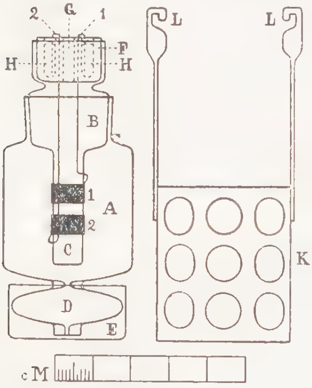

FIG. 36

The apparatus which was used for these experiments is shown in Fig. 36. It is composed of the vessel *A* made of Jena glass, containing a dipping electrode *C*. By means of a capillary, *A* is connected with the container *D* which is attached to the lower end of the tube. The glass stopper *B* is ground into *A* and is fused to *C*. Thin platinum wires are connected to the platinum electrodes 1 and 2. The wires pass through the glass wall of *C*, and also through the hard-rubber stopper *F* which is cemented into the glass stopper of the dipping electrode. The platinum wires lead to the small mercury capsules *HH*. G is a hole, and if the electrode is put under pressure, the surrounding oil passes through G into the stopper so that its various parts are all under the same pressure. The electrodes are covered with platinum black by the method of Lummer and Kurlbaum.

The apparatus is manipulated in the following manner. After the two solutions, in this case 0.02 N ethyl acetate and 0.02 N sodium hydroxide, have been mixed in specially constructed pipettes, the resulting liquid is poured into a 50 cc. beaker. *A*, which has a capacity of about 28 cc, is then dipped into the solution until *D* has been entirely filled and *A* but partly. It is then removed from the beaker, the lower end of the capillary is closed by placing a finger over it and *A* is filled full. The stopper *B* is put into place. The whole apparatus is then placed into the basket-like contrivance *KLL*. made of a copper-zinc alloy, which contains a small glass dish of mercury. The mercury acts as a seal for the lower capillary of *D*. The basket *KLL* is attached to the cover of the pressure bomb, Fig. 31, in such a manner that the two thin copper wires which are soldered to the binding posts on the cover of the bomb dip directly into the mercury filled cups *HH*. The purpose of the bulb *D* is to prevent the entrance of mercury into that part of the apparatus containing the electrodes. Naturally the presence of mercury within the conductivity apparatus would materially effect the resistance. Since the compressibility coefficient of the reaction mixture at 1500 atmospheres, the highest pressure attained, amounted to 39.9×10^{-6}, the volume change of the liquid in *A* was equal to $1500 \times 39.9 \times 10^{-6} \times 28 = 1.7$ cc. As *D* had a capacity of 3 cc., the mercury could not enter *A*.

After the apparatus has been placed under pressure and allowed to assume, after dissipation of the heat of compression, the temperature of the experiment, which was 2.4°C for the saponification of the ester, the resistances, W_1, W_2W_3, ... of the reaction mixture are measured at the times t_1, t_2, t_3 . . . . by aid of which the corresponding concentrations could be had by reference to the curves mentioned above. In the various experiments $t_2 - t_1 = 60$ minutes. The results which were obtained are given in the following table.

TABLE V

The Velocity of Saponification of .01 N. Ethyl Acetate by 0.01 N. Sodium Hydroxide at 2.40°C and various Pressures.

Pressure in Atmospheres	Concentration $C \times 10^5$	k Calculated from C_1 and C_2 by the electrical method.	k Determined by titration.	Percentage Influence of Pressure
1	C_1 393	1.22		
	C_2 305			
	C_1 398	1.21	1.22	——
	C_2 309			
500	C_1 354	1.37	1.35	11.9
	C_2 274			
1000	C_1 357	1.53	1.52	25.5
	C_2 269			
1500	C_1 339	1.67	1.67	37.4
	C_2 253			

The values for *k* given in the fourth column were determined by another method. The close numerical agreement leaves nothing to be desired. These measurements show that the rate of saponification increases directly with the pressure, so that at 1500 atmospheres the reaction proceeds 37 per cent. faster than at one atmosphere.

The effect of pressure upon the reaction

$$5\ HBr + HBrO_3 = 3\ Br_2 + 3H_2O$$

was studied by A. L. Th. Moesveld in identically the same manner, but at four different temperatures, 1.04°, 15.04°, 25.04° and 39.04°C. The individual details of this investigation may be found in the original article. However, let me emphasize the fact that this is a quadrimolecular reaction which probably proceeds according to the following equations:

$$H^+ + Br^- + H^+ + BrO_3^- = HBrO + HBrO_2 \quad \ldots (1)$$

$$\left.\begin{array}{l} HBrO + HBr = Br_2 + H_2O \\ HBrO_2 + 3\ HBr = 2\ Br_2 + 2\ H_2O \end{array}\right\} \quad (2)$$

Reaction 1 goes very slowly, whereas 2 takes place at high speed.

In this case the concentration may easily be deduced from the conductivity of the reaction mixture. It is unnecessary to plot a known graph depicting the relationship between conductivity and concentration as must be done where one ion is simply replaced by another. At the completion of this reaction ions are no longer present, only bromine and water. Since both acids are practically entirely dissociated at the dilution employed—hydrobromic acid 0.05 N. and bromic acid, 0.0102 N. and as neither causes a repression of the ionization of the other, and furthermore, since the percentage dissociation does not change appreciably in the course of the reaction during which the concentration falls by two-thirds, we may make the assumption that the fall in conductivity is a linear function of the concentration and that zero conductivity will be obtained when the concentration is zero. Special measurements showed that bromine, even in the presence of bromide ions, exerted no influence upon the conductivity of hydrobromic acid solutions.

In regard to the calculations which must be made in order that the value for *k* may be derived from the measured resistances of the reaction mixture, we know that the equation $dx\ dt = k\ (A - x)^4$ is applicable to quadrimolecular reactions, providing the reactants are present in equimolecular proportions. *A* represents the initial concentration and *x* the amount transformed at the time *t*.

Thus, $$k = 1/3\ \frac{1}{t_n - t_o}\left\{\frac{1}{(A-x)^3} - \frac{1}{A^3}\right\}$$

The conductivities are directly proportional to the concentrations, whereas the reverse holds in respect to the resistances. Thus[87]

$$k' = \frac{1}{t_n - t_o}\left(W^3_t - W^3_o\right)$$

Of course the volumes of the solutions change if measurements are made at different temperatures, and correction factors must be introduced to do away with any errors resulting from such variations. However, these will not be discussed here in any further detail[88].

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[87] For calculations of *k* see the paper of A. L. Th. Moesveld, Zeit. physik. Chem., 103, 481 (1923).

The general results of the measurements at 25.04°C. are given below.

TABLE VI

Pressure in Atmospheres	k′ corrected	k′ average value	Percentage Influence of Pressure.
1	195.5 194.9	195.0	———
500	184.3 184.6	184.4	− 5.4
1000	174.6 175.2	174.9	−10.3
1500	166.8 166.4	166.6	−14.6

The experiments at other temperatures demonstrated that the pressure coefficient of reaction velocity varies but slightly with temperature.

If the results in Table VI be compared with those of Table V, it will at once become evident that the above case presents a marked contrast with that of the saponification, both in sign as well as in size. We may therefore conclude that pressure, as such, exerts a profound influence upon reaction velocity, irrespective of any secondary differences. In closing let me direct your attention to the fact that these results offer a method whereby the more recent theories concerning the interrelationship of radiation and reaction velocity may be controlled.

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[88] See A. L. Th. Moesveld, Zeit. physik. Chem., **103**, 486 (1923), in particular paragraph 18.

THIRTEENTH LECTURE

WE WILL now turn to a problem which is not only of interest to the chemist but also to the geologist. The question regarding the influence of pressure upon solubility has already been investigated by many throughout the last half-century[89]. Even though James Thomson[90] at a meeting of the Royal Society of London on December 5, 1861, had called the attention of scientists to the importance of such studies—"I wish now to suggest as an important subject for investigation the effect of change of pressure (hydraulic pressure) in changing the crystallizing temperature of saline or other solutions of given strengths" —it was not until 1870 that the thermodynamics of these processes were developed by Guldberg[91]. Ferdinand Braun[92] later arrived at the same results independently. Planck[93], Duhem, as well as van Laar[94] treated the thermodynamical aspects of this matter. The equation representing the influence of external but uniform pressure upon solubility is nowadays usually given in this form:

$$(\partial x/\partial \pi)_T : (\partial x/\partial T)_\pi = -T \triangle v/Q \qquad (1)$$

It is very often given the name "Braun's Law".[95]

$(\partial x/\partial \pi)_T$ is the pressure coefficient of the solubility of the dissolved substance at constant temperature; $(\partial x/\partial T)\pi$ equals the temperature coefficient of the solubility at constant pressure; T is the absolute temperature of the experiment; $\triangle v$ represents the *fictitious volume change* which accompanies the solution of a definite weight of the solute in an infinitely large quantity of the saturated solution at $T°$, and Q corresponds to the amount of heat developed under such conditions and is known as the *fictitious heat of solution* with the sign reversed.

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[89] See Ernst Cohen and W. Schut, Piezochemie kondensierter Systeme Leipzig 1919, p. 374.

[90] Proc. Royal Soc. London **12**, 538 (1863); Phil. Mag. **27**, 145 (1864).

[91] Forhandlingar i Videnskabs-Selskabet, Christiania, 1870, 35. Ostwald's Klassiker der exakten Wissenschaften, **139**, 62 (1903).

[92] Wiedemanns Annalen, **30**, 250 (1887); Zeit. physik. Chem. **1**, 258 (1887).

[93] Thermodynamik, Second Edition, Leipzig, 1905, p. 226.

[94] Zeit. physik. Chem., **15**, 466 (1895); **18**, 376 (1895).

[95] See Ernst Cohen and A. L. Th. Moesveld, Zeit. physik. Chem., **93**, 385 (1919).

Since this equation is the basis of our further discussions it might be well to explain in more detail the physical significance of the quantities Q and $\triangle v$.

The act of dissolving a substance in any convenient solvent is accompanied by a heat effect, which is usually designated as the *heat of solution* of that substance. Van Deventer and van de Stadt[96], in particular, have pointed out that this terminology has frequently led to confusion. A more exact definition is necessary in view of the fact that the quantity of heat evolved during the process of solution, say of a salt in water, is dependent upon the amount of salt already in the dissolved state, *id est*, it is a function of the concentration of the solution. If successive equal portions of any substance are introduced into a solvent, each one of these will give a different heat effect. It will be seen from this that the number of possible heats of solution is infinitely large, as each one is dependent upon the concentration of the solution into which the substance is brought.

In order to differentiate let us apply the term "*initial heat of solution*," following van Deventer and van de Stadt, to that heat change which takes place when one mole of a substance is dissolved in such a large quantity of water that further dilution of the solution causes no further heat change to take place. It is this quantity which was determined in a large number of instances by Berthelot, Thomsen, and others, and is the one usually designated as the *heat of solution*. The terms *heat of solution in a large quantity of water* or solvent, and *heat of solution at infinite dilution* are also in use. Since, as I have already emphasized above, the heat change which accompanies every act of solution is dependent upon the concentration of the solution employed, it will become evident that each individual quantity of substance dissolved up to the point of saturation will show a different heat effect. Every one of these heats of solution, with the exception of the last, is called an *intermediate heat of solution*. The sum of these intermediate heats of solution is designated as the *integral* or *total* heat of solution or the *heat of solution to the point of saturation*.

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[96] Van Deventer and van de Stadt, Zeit. physik. Chem., **9**, 34 (1892).

It is the last term of the integral heat of solution which is of particular theoretical interest. It represents the heat effect which would be observed upon the solution of one mole of a substance in a saturated solution at a given temperature. It is variously called the *fictitious*, *theoretical*, or *ideal* heat of solution. The fictitious heat of solution may therefore be defined as that heat effect which would occur if one mole of a substance were to be dissolved in an infinitely large quantity of a saturated solution of that substance.

It is this calorific quantity which plays such a important role in thermodynamics[97] and which is represented by Q in the equation given on page 107.

Deductions which are entirely analogous to those which we have made for the heats of solution may now be made for the volume changes which accompany the process of solution. Thus $\triangle v$ in the equation on page 107, or the *fictitious volume change* as it may be called, represents that change in volume which would occur upon the solution of one mole of a substance in an infinitely large quantity of a saturated solution of that substance at a given temperature. It becomes perfectly obvious that the heats of solution, as well as the volume changes, become identical in the case of sparingly soluble substances.

In connection with its derivation from both of the main laws of Thermodynamics, equation (1) is so absolutely valid that no deviations result from either the electrolytic dissociation of the solute or an association on the part of the solvent. It is extremely difficult to present an experimental proof of this law because of the fact that the measurements which must be made are fraught with extraordinary obstacles[98]. However, if it can be shown once and for all that this expression holds, it will become of great value. From this equation and by the use of values which can easily be determined experimentally at ordinary pressures, it is possible to calculate the influence of external pressure upon solubility, as equation (1) may be rewritten so that the pressure coefficient

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[97] J. D. van der Waals. Zittingsverslag Kon. Akad. van Wetenschappen te Amsterdam. Feb. 28, 1885; van't Hoff, Lois de l'Equilibre chimique. Kongl. Svenska Vetenskaps Akad. Handl. **21**, 17 (1886); Ostwald's Klassiker der exakten Wissenschaften 110. Translation by Georg Bredig, p. 55; Le Chatelier, Recherches expérimentales et théoriques sur les équilibres chimiques. Extrait des Annales des Mines, livraison Mars-Avril 1888, page 138 (Paris, Dunod); Bakhuis Roozeboom, Rec. des Trav. chim. des Pays Bas, **8**, 123 (1889)

[98] Sackur, Lehrbuch der Thermochemie und Thermodynamik, Berlin, 1922, p. 188.

$$(\partial x/\partial \pi)_T = -(\partial x/\partial T)_\pi T \triangle v/Q \qquad (2)$$

Before we consider the verification of "Braun's Law" let us take up a few of the general methods which may be employed for the experimental determination of the influence of pressure upon solubility. For the details the original articles may be consulted. In general, the preparation of saturated solutions at high pressures may be brought about in two ways. Either one employs a contrivance, firmly set in the compression bomb, by which it is possible to shake the solid substance in contact with the solvent for a certain period of time at constant temperature and pressure, or the particular part of the apparatus containing

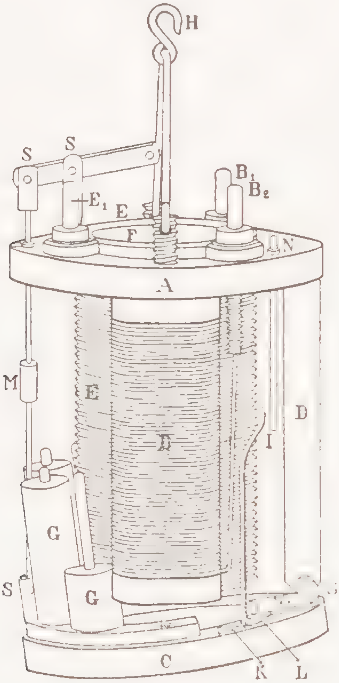

FIG. 37

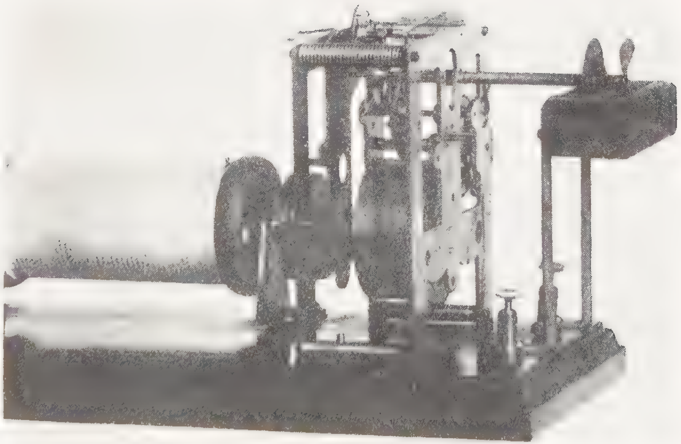

Fig. 39

both solvent and solid substance is shaken together with the bomb until the solubility equilibrium has been attained. In addition a third method, in which certain galvanic cells are used, will be taken up.

An electromagnetic stirring device, firmly set in the compression bomb, is made use of in the procedure employed by Ernst Cohen and L. R. Sinnige[99], but later improved by Katsuji Inouye, C. Euwen and Ernst Cohen.[100] I will describe this apparatus, Fig. 37, very briefly. Two iron rods, *B* are screwed tightly into the iron ring *A*. These are wound with insulated copper wire. The ends of the wires are soldered to the copper pieces B_1 and B_2. If an electric current be sent through the wire, the armature which is attached to the hard rubber ring *C* will be attracted. By means of the movable hinge *S*, *C* is connected with the copper rod *D* which in turn is screwed into *A*. If the electromagnet is magnetized intermittently, *C* will be made to move up and down. From the figure it can also be seen that *SS* will alternately move up and down. In an opening at the end of *SS* may be placed a wire to which a frame work of platinum wire (Fig. 38) may be attached.

TABLE VII

Solubilities of Mannite in gms/100 gms. water at 24.05°C.

Pressure in Atmospheres	Time of Contact and Stirring	Solubility	Average Solubility	Milligrams Mannite per gm. saturated solution
1	3	20.64	20.66	171.22
1	5	20.67		
250	4	20.95	20.92	173.01
250	6	20.89		
500	4	21.10	21.14	174.51
500	6	21.19		
1000	4	21.41	21.40	176.28
1000	6	21.38		
1500	4	21.64	21.64	177.90
1500	6	21.63		

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[99] Ernst Cohen and L. R. Sinnige, Zeit physik. Chem., 67, 432 (1909).

[100] Katsuji Inouye, C. Euwen and Ernst Cohen, Zeit. physik. Chem. 75, 257 (1910).

This latter part of the apparatus is encased in linen giving the whole the appearance of a bag into which may be placed the solid whose solubility is to be determined.

An alternating current is supplied to the electromagnet by an interpreter, such as the one illustrated in Fig. 39, which is run by means of a clock mechanism. The small bag will be caused to move up and down. It is suspended in the small glass vessel *F*, Fig. 40, which is placed between the rings *A* and *C*, Fig. 37. The apparatus hangs surrounded by oil in a pressure bomb, which in turn is suspended in a thermostat. A resistance thermometer attached to the electromagnetic stirring device makes possible an accurate control of the temperature of the solution.

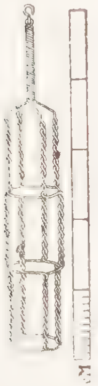

FIG. 38

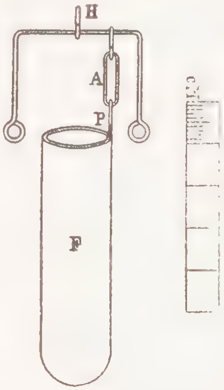

FIG. 40

The disadvantage in this method lies in the fact that the pressure at which the saturation has been allowed to take place must be reduced before a sample can be withdrawn for analysis. However, it was found in many cases that no displacement of the solubility equilibrium took place provided the necessary manipulations were carried out quickly.

I might add that the apparatus, Fig. 37, was fitted with an electrical contrivance which enabled us to control at the outside of the bomb whether or not the stirring device was functioning properly.

It will be seen from Table VII, in which the solubilities of mannite at 24.05°C. and at various pressures are given, that the procedure described above yielded very good results.

From these values, the relation of the solubility, x, of mannite in grams per hundred grams of water at 24.05°C. to the pressure π may be represented by the equation

$$x = 20.65 + 0.000931\pi - 0.0000001806\pi^2$$

FOURTEENTH LECTURE

A METHOD for the direct determination of the solubility of a substance under pressure, in which the compression bomb itself is shaken, has been described by H. F. Sill[101]. It has been refined in various ways in my laboratory[102]. The principle upon which it is based is the following: The system to be investigated, such as salt and water, is shaken at constant temperature in a specially constructed pipette which is contained in a rocking compression bomb. In the latter the pressure can be kept constant for an indefinite length of time. Some mercury which constantly flows back and forth in the pipette keeps the system well-stirred. As soon as the solubility equilibrium has been established, the resulting saturated solution is filtered at constant pressure and transferred to another pipette. After such a saturated solution has been separated from the excess of *Bodenkörper*, the pipette containing the filtrate is removed from the bomb, its contents analyzed, and the solubility of the substance at the corresponding pressure is calculated. Fig. 41 (1) shows the rocking bomb used in these experiments. It consists of a U-shaped tube made of a single piece of axle-steel. Soldered joints are to be avoided, as the bomb is partially filled with mercury. By means of a motor and a transmission this bomb, whose contents are held at constant pressure, may be made to undergo a rocking motion in an oil thermostat. In so doing the two side-arms *A* and A^1 reach an angle of approximately 10° below the horizontal in their extreme positions. The steel rod *K* is placed in the side arm *A* in order to reduce the quantity of mercury now in the bomb. *D* is the axis around which the bomb shakes when it is kept in movement by the rod *B*. The Figs. 42 and 43, show the whole set-up of the apparatus. You will notice that the bomb pictured in these is somewhat different from that in Fig. 41. However, the latter was actually employed in the experiments which I am about to describe.

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[101] H. F. Sill, J. A. C. S., **38**, 2632 (1916).

[102] Ernst Cohen and A. L. Th. Moesveld, Zeit. physik. Chem., **93**, 385 (1919); Ernst Cohen, D. H. Peereboom Voller and A. L. Th. Moesveld, Zeit. physik. Chem., **104**, 323 (1923); Ernst Cohen, Wilhelma A. T. de Meester and A. L. Th. Moesveld, Zeit. physik. Chem., **114**, 321 (1924).

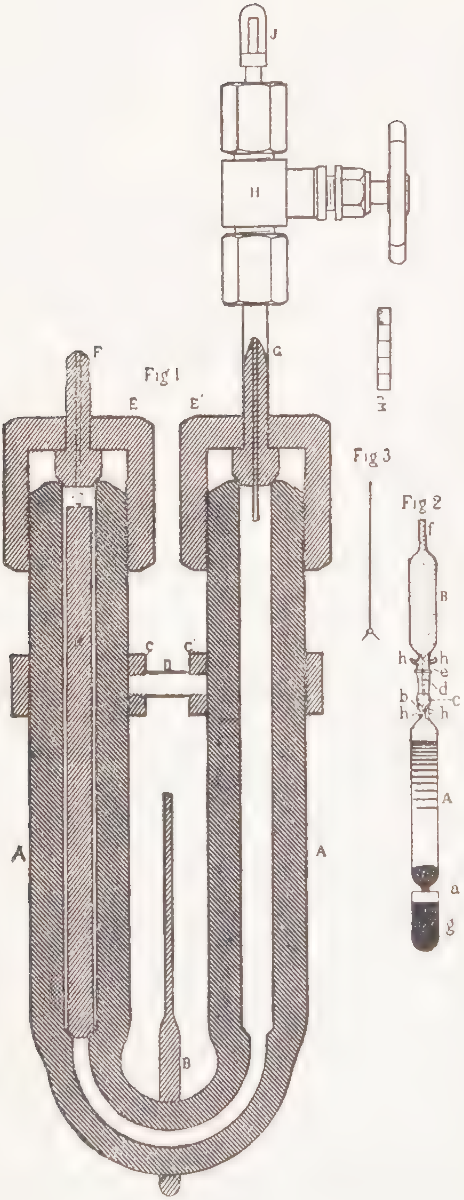

FIG. 41

Although I shall refer you to the original articles for constructional details, I would call your attention to the fact that the capillary tube which connects the pressure pump with the mercury in the bomb is wound in spiral fashion like a watch-spring. If the bomb be rocked on its axis, the pressure capillary will wind and unwind itself like a watch-spring. Fig. 43 shows how the bomb, which weighs about 40 kilograms, may be immersed or lifted from the thermostat. If the saturated solution were to be prepared in an ordinary pipette which was directly connected with the steel capillary *G* of the bomb, Fig. 41, the solution in it would mix with the saturated one when the liquid was being forced from the pipette at the conclusion of the experiment. Furthermore, the concentration of the solution in the steel capillary would be different from that of the saturated solution, as it

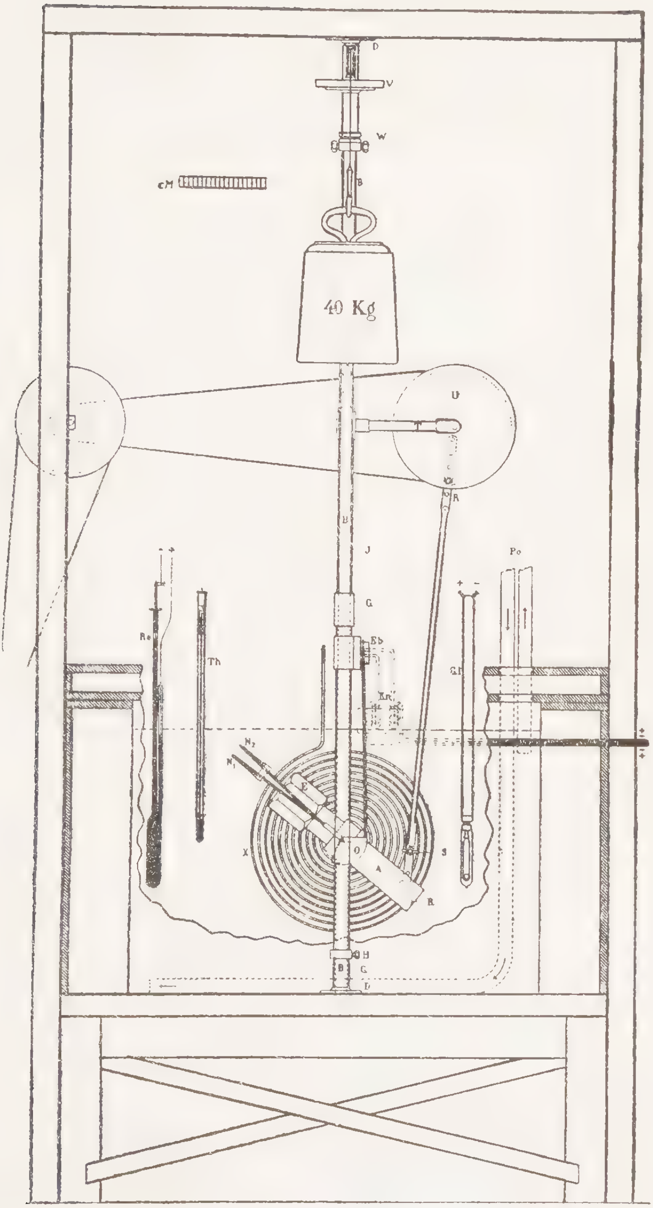

FIG. 42

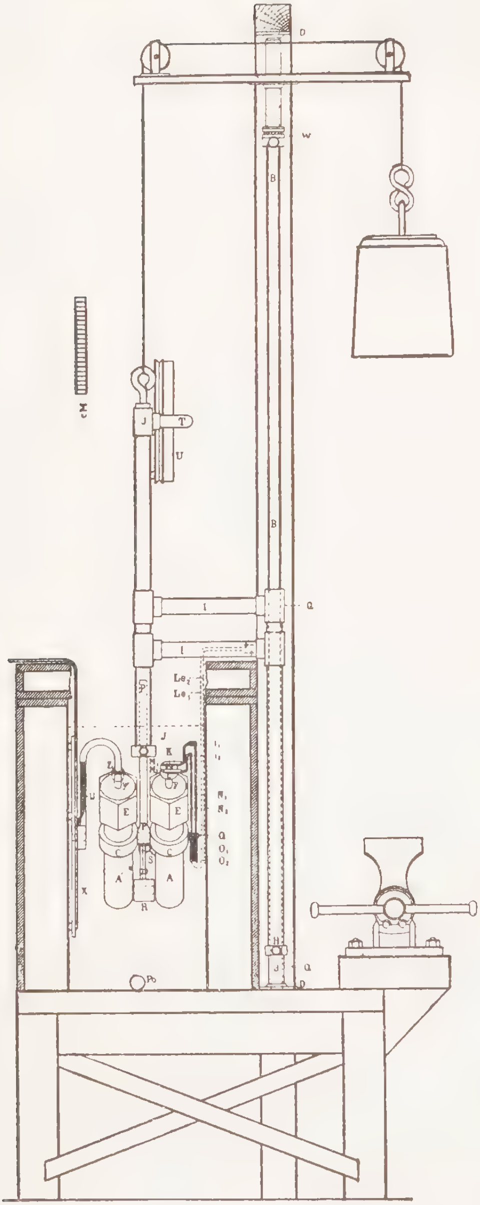

FIG. 43

would be impossible for the *Bodenkörper* to come in contact with the solvent in the tube during the process of shaking. To avoid this possible error the solubility pipette pictured in Fig. 41 (2) was constructed. It really consists of two pipettes, *A* and *B*, whose capacities approximate 15 and 9.5 cc. respectively. The bulb-shaped part *C* contains a cotton pad. *C* ends in the ground glass joint *ed*, into which *e*, actually the lower part of the pipette *B*, fits tightly. *A* terminates in the capillary *a*, whose diameter is about one millimeter. Steel wires which pass around the hooks *hhhh* may be used to firmly join the two pipettes together. The capillary *a* is immersed in a capsule *g* filled with mercury in which it is held fast by a cork stopper. The latter is notched in such a manner that after the pipette has been set into the bomb, the mercury in the capsule is at all times in contact with that in the bomb. During the course of the experiment, *f* is connected by means of a rubber tube with the steel capillary *G*. Care should be taken that *f* fits tightly to the metal tube.

For the details of manipulation, reference may be had to the original publications. It seems to me, however, highly advisable to say something concerning the method by which the saturated solution may be withdrawn from the pipettes, an operation which is peculiar to this experimental procedure. The steel tube *G*, which projects from *E′* is connected by means of a short, thin rubber tube with a small graduated pipette *P* in such a manner that the metal and glass tubes closely adjoin each other. The capacity of this pipette, which is not pictured in the illustration, is approximately that of *B*. The stopcock *H* of the bomb is carefully opened, and at the same time a second person continually watches the gauge on the pressure pump, Fig. 32, and sees to it that the pressure remains equal to that at which saturation was permitted to take place, for instance 1500 Atm. This he does by forcing oil into the pressure transmission whenever necessary. Vaseline, which had been placed in *G* before the beginning of the run, next enters the pipette *P*; then follows benzene with which the pipette *B* had been filled before the experiment. When a quantity of benzene equivalent to the capacity of *B* has been forced into *P*, we may then know that the saturated solution has, at 30.00°C. and 1500 Atmospheres, been filtered through the cotton pad and has passed, along with the benzene originally present in *A* over the solution, from *A* into *B*. The benzene now floats over the filtered saturated solution in *B*. The stopcock *H* is then closed and the pressure transmission *F*, which carries oil over into the compression bomb, is immediately opened so that the pressure quickly drops to one atmosphere.

This adiabatic reduction of pressure causes the saturated solution in *B* to expand, in consequence of which a slight amount of the liquid is forced back into *A*. At the same time a certain quantity of salt crystallizes out in *B* because of the release of pressure and the resulting fall in temperature. The process of crystallization requires some time, and before it occurs the expansion of the saturated solution as well as its displacement into *A* has stopped. The percentage composition of the system in *B* is therefore that of the solution saturated under pressure.

The compression bomb is then opened; the lock *E'* is removed so that the solubility pipette which floats on the mercury in the bomb comes out; the capsule *g* is taken out; *a* is closed by placing a finger over the opening; traces of mercury sticking to the rubber tube are carefully removed by a piece of cotton padding to avoid its entrance into *B* and consequent contamination of the contents; the pipettes *A* and *B* with the capsule *g* are taken out after *f* has been closed by a finger. After the ground glass joint *d* has been cleaned, it is closed by a small glass cap.

Any crystals which may have formed in *B* are made to dissolve by heating the solution in the pipette. A specially constructed stirrer of platinum wire, Fig. 41 (3), is employed to hasten the process of solution. If this latter device is rotated rapidly between the thumb and the index finger, the platinum leaves will spread apart and cause a

TABLE VIII

Solubility of Thallous Sulphate at 30.00°C. and various Pressures

Pressure in atmospheres	Time of shaking in hours.	Gms. Tl_2SO_4 in 100 gms. of the saturated solution	Average Found	Average Calculated from equation A	Average Calculated from equation B
1	19 (+)	5.83	5.83	5.83	5.83
1	18 (−)	5.83			
500	19-1/4 (+)	7.50	7.48	7.48	7.45
500	18-1/4 (−)	7.46			
1000	20 (+)	9.12	9.03	9.03	9.02
1000	23-1/2 (−)	8.94			
1500	24-1/4 (+)	10.53	10.50	10.50	10.53
1500	19-1/3 (−)	10.48			

thorough mixing of the saturated solution. Upon complete solution of all the solid matter the benzene is removed and the remaining solution is analyzed. Some of the results obtained by this method are summarized in Table VIII.

Several explanatory remarks may be made concerning the results in the above table. The signs (+) and (−) in the second column indicate respectively whether the solubility equilibrium was attained from an unsaturated or a supersaturated solution.

The figures noted in the fifth column were calculated from the equation

$$x = 5.831 + 0.003377\pi - 0.000000175\pi^2. \quad . \quad . \quad .(A).$$

This expression was deduced from the experimental results by the method of least squares.

The values given in the last column were derived from the equation

$$x = 5.831 + 0.003295\pi - 0.000000190\pi^2.$$

This expression represents the results obtained by Ernst Cohen and J. C. van den Bosch[103] indirectly by the measurement of the conductivity of the saturated solutions. I will not discuss this procedure at the present time.

However, I should like to call your attention to another indirect procedure, also electrical in nature[104], which has found application in a number of cases, particularly where the work concerned itself with the determination of the pressure coefficient of the solubilities of electrolytes. For example. If we wish to measure, at the temperature T, the pressure coefficient of the solubility of a salt which yielded in solution the cations *K* and the anions *A*, we would construct two galvanic cells according to the following diagrams:

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[103] Ernst Cohen and J. C. van den Bosch, Zeit. physik. Chem. **114**, 453 (1925).

[104] Ernst Cohen and L. R. Sinnige, Zeit. physik. Chem., **69**, 102 (1909).

Electrode reversible with respect to the Cation K.	Saturated Solution of the salt K A in contact with the solid phase of the salt at T° and one Atm. pressure.	Electrode reversible with respect to the (α–cell) Anion A
and		
Electrode reverisble with respect to the Cation K.	Saturated Solution of the salt K A at T° and 1 atm. *No* solid K A present.	Electrode reversible with respect to the (β–cell) Anion A

Now if at T° the α–cell be brought under the pressure π its E.M.F. will change for two reasons, first, because of the direct influence of pressure upon the E.M.F., and second because of the indirect influence of pressure, by virtue of the fact that solubility of the salt varies with the pressure. Since the E.M.F. is a function of the concentration, it will also change.

These conditions may be represented by the equation

$$\left[\left(\frac{\partial E}{\partial \pi}\right)_T\right]_\alpha = \left[\left(\frac{\partial E}{\partial \pi}\right)_T\right]_\beta + \left(\frac{\partial E}{\partial x}\right)_{T\,\pi} \times \left(\frac{\partial x}{\partial \pi}\right)_T$$

in which x represents the concentration of the saturated solution at T° and one atmosphere pressure. From this we may obtain

$$\left(\frac{\partial x}{\partial \pi}\right)_T = \frac{\left[\left(\frac{\partial E}{\partial \pi}\right)_T\right]_\alpha - \left[\left(\frac{\partial E}{\partial \pi}\right)_T\right]_\beta}{\left(\frac{\partial E}{\partial x}\right)_{T.\pi}} \quad \ldots\ldots\ldots (1)$$

which signifies that the pressure coefficient of the solubility is equal to the difference of the pressure coefficients of the electromotive forces of the α– and β–cells, divided by the concentration coefficient of the electromotive forces of the cells under investigation.

In determining the pressure coefficient of the solubility of thallous sulphate at 30.00°C., Ernst Cohen, Fusao Ishik-

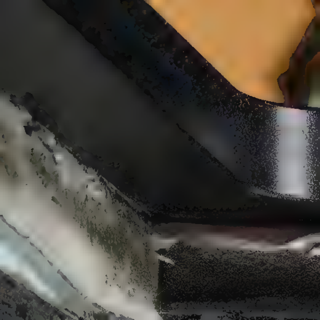

TABLE X

Temperature 30.00°C. E.M.F. of the β cells in volts.

Pressure in Atmospheres	Cell I	Cell II	Average value Found	Calculated	Difference of calculated and experimental values in volts
1	1.05858	1.05854	1.05856	1.05856	0
500	1.06469	1.06458	1.06464	1.06463	−0.00001
800	1.06792	1.06775	1.06783	1.06783	0
1200	1.07160	1.07155	1.07158	1.07163	+0.00005
1500	1.07420	1.07402	1.07411	1.07409	−0.00002

From these results the equation

$$E_\beta = 1.05856 + 0.00001301\ \pi - 0.000000001773\ \pi^2 \quad (2)$$

may be derived by the method of least squares. Comparison of the fourth and fifth columns of the above table demonstrates the validity of this expression. Thus, we obtain from (2):

$$\left[\left(\frac{\partial E}{\partial \pi}\right)_T\right]_\beta = +0\ 00001301 \text{ volt atmospheres.}$$

To ascertain the value of the differential $(\partial E\ \partial x)_{T.\pi}$ in equation (1) the E.M.F. of a β type cell was measured, in which the concentration of Tl_2SO_4 varied. The numerical data are given in Table XI.

TABLE XI.

Temperature 30.00°C. E.M.F. of β cells containing solutions of varying concentrations

Concentration in gms. per 100 gms. solution	Cell I	Cell II	Mean Value Found	Calculated	Difference of calculated and experimental values in volts
2.283	1.08234	1.08236	1.08235	1.08204	−0.00031
3.059	1.07475	1.07484	1.07479	1.07515	+0.00040
4.104	1.06760	1.06738	1.06749	1.06748	+0.00001
5.110	1.06181	1.06177	1.06179	1.06168	−0.00011
5.826	1.05855	1.05846	1.05850	1.05853	+0.00003

By the method of least squares we find

$$E_x = 1.10771 - 0.01305\ x + 0.0007907\ x^2 \qquad (3)$$

A glance at the figures in columns four and five brings out the correctness of this equation.

From Equation (3)

$$\left[\left(\frac{\partial E}{\partial x}\right)_{T.\pi}\right]_{x\,=\,5.286} = -\ 0.00384 \text{ volts/per cent.}$$

If the experimentally determined values for $\left[\left(\frac{\partial E}{\partial \pi}\right)_T\right]_\alpha$, $\left[\left(\frac{\partial E}{\partial \pi}\right)_T\right]_\beta$ and $\left(\frac{\partial E}{\partial x}\right)_{T.\pi}$ be substituted in equation (1), the pressure coefficient of the solubility of thallous sulphate at 30° may be calculated.

$$\left(\frac{\partial x}{\partial \pi}\right)_{30.00^\circ} = \frac{0-0.00001301}{-0.00384} = +0.00339 \text{ per cent/atmospheres.}$$

Of course this method for the determination of the pressure coefficient of the solubility can only be applied in those cases where it is possible to construct a galvanic cell similar to the one represented schematically on page 120. For non-electrolytes it will always be necessary to follow the direct method for the determination of the solubilities at various pressures.

FIFTEENTH LECTURE

NOW that we have seen how the differential $(\partial x/\partial \pi)_T$ in equation (1)* may be ascertained, let us turn next to the determination of $(\partial x/\partial T)_\pi$. This value may be obtained by carrying out solubility measurements of a given substance in the desired solvent at various temperatures. Using the method of least squares, the coefficients of an equation are ascertained which represents the experimentally determined solubilities as functions of the temperature. Differentiation of this equation with respect to *T* then yields the value for $(\partial x/\partial T)_\pi$. Concerning the technique of solubility determinations nothing further need be said at this time as I presume you are acquainted with it. However, let me call your attention to a very useful apparatus[106], Fig. 45, which was copied after one described by A.A. Noyes[107]. The flasks containing the solid and the solvent are placed in the rings *AA* of the apparatus and held tightly by means of the screws *BBB*. These rings are attached to a shaft *D* which passes through a stuffing box *N* and ends in a copper container which hold the cog wheels *EE*. The vessel is filled with vaseline. The shaft *G*, which passes through the tube *F*, the latter

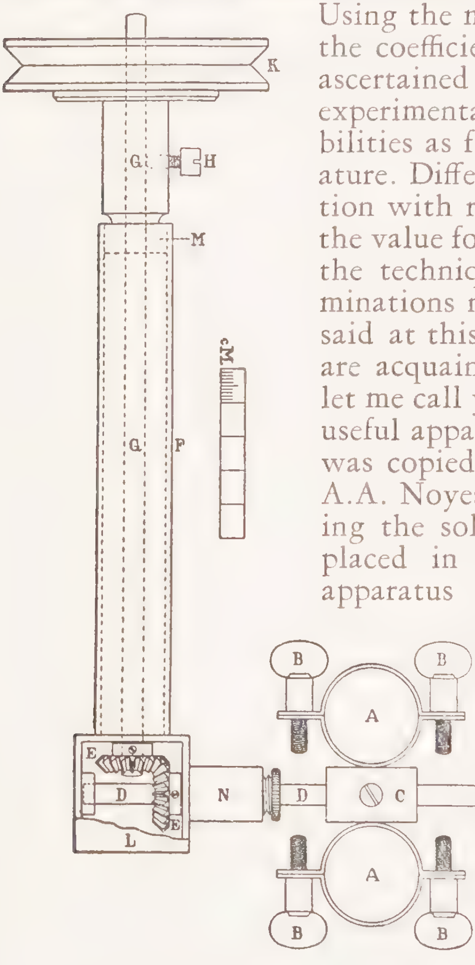

FIG. 45

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* See page 107.

[106] Ernst Cohen and H. R. Bruins, Zeit. physik. Chem., 93, 43 (1918).

[107] A. A. Noyes, Zeit. physik. Chem., 9, 602 (1892).

being clamped to a stand, may be put into rotation by a motor. The whole apparatus is immersed in a thermostat filled with water or oil, the temperature of which may be kept constant within one hundredth of a degree.

The method of analysis of the saturated solution is of course dependent upon the properties of the material under investigation.

We shall next concern ourselves with the determination of the fictitious heat of solution Q in equation (1) on page 107. Three methods will be taken up, two of which are based upon electrochemical measurements. Two other electrochemical procedures have also been employed, but the literature may be consulted in these cases[108].

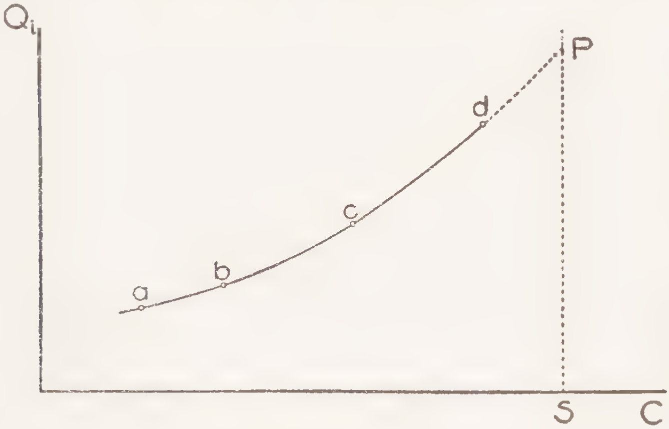

FIG. 46

You will remember that the fictitious heat of solution of a substance in a given solvent may truly be regarded as the "last intermediate heat of solution" since it deals with the heat effect which would result if one mole of a substance were dissolved in an infinitely large quantity of a saturated solution of that material at the temperature of the experiment.

If, at a given temperature, one determines the intermediate heats of solution as a function of the concentration of the solution in which the said substance is being dissolved then the point of intersection *P*, Fig. 46, of the curve *abcd*. . . ., which represents the intermediate heats of solution, and the ordinate (S) which corresponds to the concentration of the saturated solution, will give the fictitious heat of solution. This procedure gives accurate results only when it is possible to determine the intermediate heats of solution up to a concentration very close to the saturation point, since then extrapolation over a short range only is required. In most cases this cannot be done, since the rate of solution decreases decidedly as the concentration increases. In the ordinary calorimetric process such a state of affairs would entail too great a temperature correction.

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[108] Ernst Cohen and H. R. Bruins, Zeit. physik. Chem., **93**, 43 (1918).

In two cases, however, it was possible by calorimetry to measure the intermediate heats of solution near the saturation point and by slight extrapolation to arrive at the fictitious heat of solution. The system meta-dinitrobenzene-ethyl acetate was found to be amenable to such treatment and was studied from this point of view by Ernst Cohen and A. L. Th. Moesveld[109]. We shall have occasion to look into this matter further. The second case had to do with the system ammonium nitrate and water. In my ninth lecture I discussed this substance in some detail, particularly in regard to the heat of transition of ammonium nitrate III into modification IV*. We also saw that the intermediate heats of solution of modification IV at 32.3°C. could be represented as a function of the concentration of the solution by the equation

$$Q_{IV} = -5910 + 83.057c - 0.73476c^2 + 0.00224c^3$$

If we substitute for *c* the experimentally determined value 70.93[110] for the concentration of the saturated solution at 32.3°C., we obtain for the fictitious heat of solution of ammonium nitrate IV at 32.3°C.

$$(Q_f)_{IV} = -2917 \text{ gram calories/mole}$$

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[109] Ernst Cohen and A. L. Th. Moesveld, Zeit. physik. Chem., **93**, 385 (1919), particularly paragraph 93.

* See page 81.

[110] Ernst Cohen and J. Kooij, Zeit. physik. Chem., **109**, 81 (1924); Ernst Cohen and H. L. Bredée, ibid, **117**, 143 (1925).

In exactly the same way the fictitious heat of solution of modification III at 32.3°C. is found from the equation

$$Q_{III} = -5510 + 83.0571c_1 - 0.73476c^2 + 0.00224c_1^3$$

to be*

$$(Q_f)_{III} = -2517 \text{ gram calories/mole}$$

Let me add in this connection that the intermediate heats of solution* of ammonium nitrate can be determined calorimetrically until the concentration is sixty-nine per cent. Since the concentration of the saturated solution is about seventy-one per cent., only a slight extrapolation is necessary and consequently the accuracy of the calculated fictitious heat of solution is of a high order.[111]

Let us now turn to a discussion of the two electrical procedures for the determination of the fictitious heat of solution, of which mention was made on page 125.[112] Suppose, for example, that we wish to determine this quantity in the case of an electrolyte which on solution yields the cations, *K* and the anions *A*. We shall therefore consider the following galvanic cells:

Electrode reversible with respect to the cation K	Saturated solution of the salt KA in contact with the *Bodenkörper* at T°	Electrode reversible with respect to the anion A	(α cell)

and

Electrode reversible with respect to the cation K	Saturated solution of the salt KA at T° No *Bodenkörper* present	Electrode reversible with respect to the anion A	(β cell)

Since both cells are reversible we may apply the Gibbs-Helmholtz equation to them. For the α cell we obtain

$$(E_e)_\alpha = (E_c/n\epsilon)_\alpha + T\,(dE/dT)_\alpha$$

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* See page 84.

*See Table IV, page 83.

[111] For a check method on the experimental values of Q_f see Ernst Cohen and H. L. Bredée, Zeit. physik. Chem., **117**, 143 (1925).

[112] Ernst Cohen and H. R. Bruins, Zeit. physik. Chem., **93**, 43 (1918).

in which E_e and E_c represent, respectively, the electrical and chemical energies of the system, n is the valence of either ion, and ϵ is the number of coulombs which is carried by one gram equivalent of either ion.

For the β cell we may write

$$(E_e)_\beta = (E_c/n\epsilon)_\beta + T\,(dE/dT)_\beta \qquad (2)$$

Since the solutions in the α and β cells are both saturated at T_o°, we may write at this temperature

$$(E_e)_\alpha = (E_e)_\beta.$$

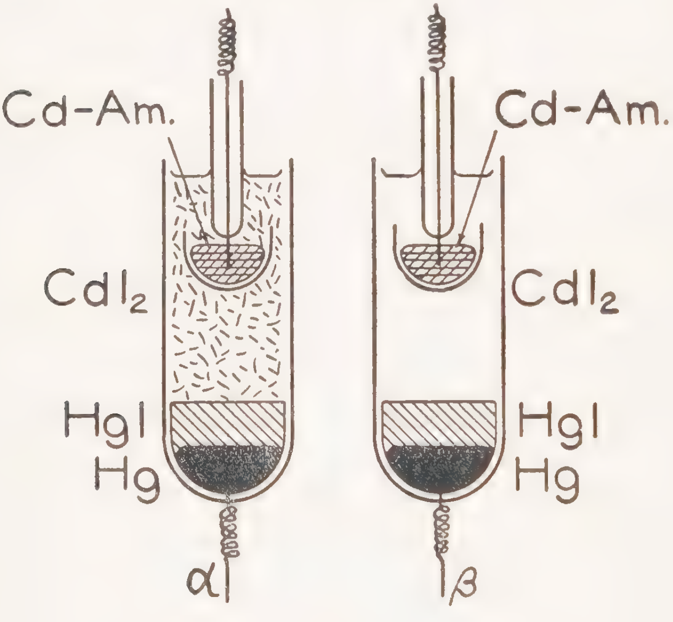

Fig. 47

Substituting their equals we find that

$$(E_c/n\epsilon)_\alpha + T_o\,(dE/dT)_\alpha = (E_c/n\epsilon)_\beta + T_o\,(dE/dT)_\beta$$

$$(E_c/n\epsilon)_\beta - (E_c/n\epsilon)_\alpha = T_o[(dE/dT)_\alpha - (dE/dT)_\beta] \qquad (3)$$

The meaning of the left member of this equation will become clear to you upon consideration of the meachanism of the reactions which take place in the cells. This may most easily be done by studying a special case, such as that of the fictitious heat of solution of cadmium iodide at 18°C. The cells, Fig. 47, to be investigated take the following forms:

Cadmium amalgam Ten per cent. by weight	A solution of cadmium iodide saturated at 18°C., in contact with *Bodenkörper*	HgI − Hg (α cell)

and

Cadmium amalgam Ten per cent. by weight	A solution of cadmium iodide, saturated at 18°C. without *Bodenkörper*	HgI − Hg (β cell)

If the two cells are connected against each other, and if at T_0° (273.09 + 18°) 2 × 96494 coulombs are allowed to pass through them, a series of reactions will take place. Thus in the β cell:

1) One gram atom of cadmium is withdrawn from the amalgam. This reaction is accompanied by a heat effect which may be designated as W_1.

2) One mole of cadmium iodide is formed. Heat effect, W_2.

3) One mole of mercurous iodide is decomposed. Heat effect, W_3.

4) The mole of cadmium iodide which has been formed dissolves in the solution saturated at T_0°. The heat change which accompanies this process is the fictitious heat of solution of cadmium iodide at the temperature of the experiment. It may be designated by the symbol $(F)_{T_0}$.

Simultaneously, the following reactions take place in the α cell:

1a) One gram atom of cadmium is added to the amalgam. Heat effect, $-W_1$.

2a) One mole of cadmium iodide is decomposed. Heat effect, $-W_2$.

3a) One mole of mercurous iodide is formed. Heat effect, $-W_3$.

4a) One mole of cadmium iodide is withdrawn from the saturated solution at $T_0°$. Heat effect, $-(F)_{T°}$.

5) One mole of cadmium iodide dissolves in the saturated solution at $T_0°$. Heat effect $+ (F)_{T°}$.

Thus the chemical energy of the system $(E_c)_\beta - (E_c)_\alpha$ equals $+ (F)_{T_0}$.

From equation (3) on page 128,

$$+(F)_{T_0} = T_0 [(dE/dT)_\alpha - (dE/dT)_\beta] 2 \times 96494 \times 0.2389 \text{ gram calories} \quad (4)$$

To calculate $(F)_{T_0}$ it is, therefore, only necessary to determine the temperature coefficients of the α and β cells at T_0 and to substitute these experimental values in the equation. This was done in the case of the cells outlined above and the experimental details may be found in the original articles. The results are summarized in Table XII.

TABLE XII

Temperature	α cells		β cells	
C.°	Observed	Calculated	Observed	Calculated
16.016	0.41385	0.41385	0.41365	0.41366
18.000	0.41459	0.41459	0.41458	0.41457
20.025	0.41533	0.41533	0.41558	0.41550
22.032	0.41606	0.41606	0.41642	0.41642
23.958	0.41675	0.41675	0.41730	0.41730

The temperature formulae which may be deduced from these results follow:

For the α cells: $(E_\alpha)_{t°} = 0.40782 + 0.0003869t - 0.0000005775t^2$ (5)

For the β cells: $(E_\beta)_{t°} = 0.40631 = 0.0004590t$ (6)

From (5) we get $\left[\left(\frac{dE}{dT}\right)_\alpha\right]_{18°.0} = +0.0003661$ Volt degree

From (6) we get $\left[\left(\frac{dE}{dT}\right)_\beta\right]_{18°.0} = +0.0004590$ Volt degree

On substituting these values in (4) we find that

$(F)_{18^\circ} = 291.09\,(0.0003661 - 0.0004590)\,2 \times 96494 \times 0.2389 = -1246$ gram calories/mole.

That the fictitious heat of solution of cadmium iodide is negative, checks very well, on the basis of the Principle of Movable Equilibrium, with the fact that the solubility of this compound increases with the temperature.

The basis of the second electrical method for the determination of the fictitious heat of solution rests on the following consideration. If the temperature of an α cell be varied, its E.M.F. will change for two reasons; first, because of the direct influence of temperature upon E.M.F., and second in view of the fact that the solubility of the *Bodenkörper* changes with the temperature. As the E.M.F. is a function of the solubility, any change in the latter will cause a corresponding variation in the former.

Thus, the temperature coefficient of the α cell may be represented by the expression

$$(dE/dT)_\alpha = (dE/dT)_\beta = (dE/dx)_T\,dx/dT \qquad (7)$$

where x stands for the solubility.

If the value for $(dE/dT)_\alpha$ be introduced into (4) we find that

$$(F)_{T_0} = [T_0\,(dE/dx)_{T_0}.dx/dT]\,2 \times 96494 \times 0.2389 \text{ gram calories.} \qquad (8)$$

For the experimental determination of the fictitious heat of solution by this method the values of $(dE/dx)_{T_0}$ and dx/dT at T_0° must be gotten.

Measurements of the E.M.F. of cells containing solutions of cadmium iodide of varying strength showed that

$$E_{18^\circ.0} = 0.43150 + 0.000283\,x - 0.00001428x^2 \qquad (9)$$

From this we may derive that

$$(dE/dx)_{18^\circ.0} = -0.001023 \text{ volt/per cent.}$$

The solubility of cadmium iodide in grams per hundred grams of the saturated solutions was ascertained for various temperatures. This gave the expression

$$x = 44.18 + 0.0828t + 0.000183t^2 \qquad (10)$$

from which it may be seen that

$$(dx/dT)_{18^\circ.0} = - +0.08939 \text{ grams/degrees.}$$

If these values be substituted for (dE/dx) and (dx/dT) in equation (8), the results will show that the fictitious heat of solution of cadmium iodide at 18°.0C. is equal to

$(F)_{18^\circ.0} = - 291.09 \times 0.001023 \times 0.08939 \times 2 \times 96494 \times 0.2389 = -1227$ gram calories/mole.

The first electrical procedure gave −1246 gram calories/mole as the calculated value.

For cadmium iodide at 30°.0C. the first electrical method gave −1359 gram calories/mole[113], the second −1340 gram calories/mole.

At the same temperature the fictitious heat of solution of thallous sulphate[114] was found to be −7435 and −7440 gram calories/mole.

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[113] Ernst Cohen, C. W. G. Hetterschij and A. L. Th. Moesveld, Zeit. physik. Chem., **94**, 210 (1920).

[114] Ernst Cohen, Fusao Ishikawa and A. L. Th. Moesveld, Zeit. physik. Chem., **105**, 155 (1923).

SIXTEENTH LECTURE

WE HAVE yet to find out how the fictitious volume change, represented by Δv in Braun's Law*, may be determined. To do so it will be necessary to express this quantity in such a way that it may become susceptible of experimental treatment.[115]

If the concentration expressed in grams of solid per gram of solution, of one gram of solution be increased from x to x+dx by the addition of the calculated quantity of solid material, p grams, the weight of the resulting solution will naturally become 1+p grams. The liquid will thus contain (1+p) (x+dx) grams of solid in solution. The increase in weight of the solid may be expressed algebraically as

$$(1+p)(x+dx) - x = p$$

$$p = dx/1-x-dx,$$

and

$$1+p = 1-x/1-x-dx.$$

If the specific volume of the solution be represented by v_x when the concentration is x, and v_{x+dx} when it has become x+dx, the volume change of the solution may be expressed as

$$\frac{1-x}{1-x-dx} \cdot v_{x+dx} - v_x \tag{1}$$

The volume of the solid material disappearing in solution has not been taken into account in this expression. If we substitute

$$v_{x+dx} = v_x + dv_x/dx.\, dx$$

in (1), we find that

$$\frac{1-x}{1-x-dx}(v^x + \frac{dv_x}{dx}\,dx) - v_x = (1 + \frac{dx}{1-x})\,(v_x + \frac{dv_x}{dx}dx) - v_x =$$

$$\frac{dx}{1-x}\,v_x + \frac{dv_x}{dx}\,dx.$$

However, p grams of the solid substance as such have disappeared. If the specific volume of the material be designated by v_s, the corresponding volume change may be expressed by

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* See page 107.

[115] Ernst Cohen and A. L. Th. Moseveld, Zeit. physik. Chem., **93**, 385 (1919), especially page 436.

$$-pv_s = -\frac{dx}{1-x-dx}v_s = -\frac{dx}{1-x}v_s.$$

The total volume change which accompanies the solution of $dx/1-x$ grams of the solid material is therefore

$$\frac{dx}{1-x}\left\{v_x + (1-x)\frac{dv_x}{dx} - v_s\right\}.$$

For every gram of solid which goes into solution, in which event the quantity of solution is to be construed as infinitely large, for only then would the accompanying change in concentration be negligibly small,—the volume change may be said to be

$$v_x + (1-x)\,dv_x/dx - v_s.$$

If x be made equal to the concentration of the saturated solution (x_1) at the temperature of the experiment and the prevailing pressure, this last expression will represent the desired fictitious volume change:

$$\triangle v = v_{x_1} + (1-x)\left(\frac{dv_x}{dx}\right)_{x=x_1} - v_s \qquad (2)$$

An entirely analogous expression may be constructed for the fictitious volume change per *mole* of solid substance. The specific volumes in equation (2) must then be replaced by molecular volumes, and the concentrations by molecular percentages, in which the sum of the concentrations so expressed is equal to one.

This relationship may also be deduced by the graphic method as suggested by Bakhuis Roozeboom[116].

To make clear the application of equation (2) let us consider the determination of the fictitious volume change of a saturated solution of cadmium iodide[117] at 30.00°C.

[116] Die heterogenen Gleichgewichte von Standpunkte der Phasenlehre, Braunschweig 1904, **2**, 401, 405.

[117] Ernst Cohen, C. W. G. Hetterschij and A. L. Th. Moesveld, Zeit. physik. Chem., **94**, 210 (1920), particularly page 225.

In order to obtain v_x it was necessary first of all to measure the specific volumes of solutions of cadmium iodide of varying concentrations, using a specially constructed dilatometer or pycnometer. The results secured showed that v_x could be represented as a function of x by the equation

$$v_x = 1.00435 - 0.820924\,x + 0.016857x^2$$

v_x was accordingly found to equal 0.62395 and

$$\left(\frac{dv_x}{dx}\right)_{x=x_1} = -0.80515$$

in which $x_1 = 0.46793$ represents the concentration of the saturated solution as determined by solubility measurements. The specific volume of solid cadmium iodide, as ascertained by the method of Andreae, which I took up in one of my former lectures*, was found to be $v_s = 0.17649$. Substituting these values in equation (2) we find that

$$\triangle v = 0.62395 + (1 - 0.46793) \times -0.80515 - 0.17649 = + 0.0191 \pm 0.0003 \text{ cc/gm.}$$

For a discussion of several other volumetric methods which may be employed in the determination of the fictitious volume change, the original work[118] may be consulted.

In those cases where electrolytes are being investigated from which distinctive reversible galvanic cells may be constructed, two electrical methods[119] may be applied to obtain the fictitious volume change which accompanies the act of solution.

In order to explain the first electrical method let us imagine that we are to determine the fictitious volume change of an aqueous solution of the electrolyte *KA* at T_0 and one atmosphere pressure. *K* thus represents the cation, and *A* the anion. It will first be necessary to construct two reversible galvanic cells according to the following scheme*.

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* See page 58.

[118] Ernst Cohen and A. L. Th. Moesveld, Zeit. physik. Chem., **105**, 145 (1923); Ernst Cohen, Wilhelma A. T. de Meester and A. L. Th. Moesveld, *ibid*, **108**, 103 (1924).

[119] Ernst Cohen, C. W. G. Hetterschij and A. L. Th. Moesveld, Zeit. physik. Chem., 94, 210 (1920); Ernst Cohen and A. L. Th. Moesveld, *ibid*, **105**, 145 (1923).

* See page 127.

Electrode reversible with respect to the cation K	Solution of KA, saturated at T° and one atmosphere pressure in contact with *Bodenkörper*	Electrode reversible with respect to the (α cell) anion A

and

Electrode reversible with respect to the cation K	Solution of KA, saturated at T° and one atmosphere pressure. No *Bodenkörper* present	Electrode reversible with respect to the (β cell) anion A

The equation

$$-\left(\frac{\partial E}{\partial \pi}\right)_{T.e} = \left(\frac{\partial v}{\partial e}\right)_{T.\pi} \qquad (1)$$

may be applied to these reversible galvanic cells[120]. It expresses the fact that the pressure coefficient of the E.M.F. of a reversible galvanic cell preceded by a minus sign is equal to the volume change which the current yielding system undergoes, when at constant pressure and temperature a unit quantity of electricity flows through the cell. We shall later have occasion to discuss this all-important equation in connection with another matter.

Applying this equation to the above cells we find

For the α cell: $$\left[\left(\frac{\partial E}{\partial \pi}\right)_{T.e}\right]_\alpha = \left[\left(\frac{\partial v}{\partial e}\right)_{T.\pi}\right]_\alpha \qquad (2)$$

For the β cell: $$-\left[\left(\frac{\partial E}{\partial \pi}\right)_{T.e}\right]_\beta = \left[\left(\frac{\partial v}{\partial e}\right)_{T.\pi}\right]_\beta \qquad (3)$$

Subtracting (3) from (2) we obtain:

$$\left[\left(\frac{\partial E}{\partial \pi}\right)_{T.e}\right]_\alpha - \left[\left(\frac{\partial E}{\partial \pi}\right)_{T.e}\right]_\beta = -\left[\left(\frac{\partial v}{\partial e}\right)_{T.\pi}\right]_\alpha + \left[\left(\frac{\partial v}{\partial e}\right)_{T.\pi}\right]_\beta \qquad (4)$$

The physico-chemical significance of the right hand member of the above equation becomes apparent upon consideration of the reaction mechanism of both cells when a unit quantity of electricity, 96494 coulombs, is allowed to pass through them at the temperature of saturation, T_0. If, for instance, the fictitious volume change resulting upon solution of cadmium iodide in a solution of that substance saturated at $T_0°$ is to be determined, the following equations may be deduced on the basis of the behavior of the cells as previously noted*.

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[120] J. Willard Gibbs, Trans. of the Connecticut Academy of Arts and Sciences, [2] 3, 508 (1878); P. Duhem, Le potentiel thermodynamique et ses applications, Paris, 1886, p. 117; See also Ernst Cohen and L. R. Sinnige, Zeit. physik. Chem., 67, 1 (1909).

$$\triangle v = -\left[\left(\frac{\partial v}{\partial e}\right)_{T.\pi}\right]_{\alpha} + \left[\left(\frac{\partial v}{\partial e}\right)_{T.\pi}\right]_{\beta} \tag{5}$$

and from (4)

$$\triangle v = \left[\left(\frac{\partial E}{\partial \pi}\right)_{T.e}\right]_{\alpha} - \left[\left(\frac{\partial E}{\partial \pi}\right)_{T.e}\right]_{\beta} \tag{6}$$

In order to determine the fictitious volume change experimentally we have only to ascertain the pressure coefficients of the α and β cells at the temperature $T_0°$.

The measurements on cadmium iodide at 30.00°C. gave—

For the α cells $\left[\left(\frac{\partial E}{\partial \pi}\right)_{T.e}\right]_{\alpha} = +\ 0.0000001$ volt/atm.

For the β cells $\left[\left(\frac{\partial E}{\partial \pi}\right)_{T.e}\right]_{\beta} = -\ 0.00000363$ volt/atm.

Whence, form (6)

$$\triangle v = \frac{(+0.0000001 + 0.00000363) 2 \times 96494}{0.1013 \times 366.24} = +0.0194 \pm 0.0001 \text{ cc/gm.}$$

The figure 0.1013 represents the number of joules corresponding to 1 cc-atm.[121]; 366.24 is the molecular weight of cadmium iodide. This result for $\triangle v$ checks very well with that obtained previously by the volumetric method*.

The second electrical method is based upon the fact that a very definite relationship exists between the pressure coefficients of the E.M.F. of the α and β cells.

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* See page 129.

[121] 1 cc-atm. = $13.595 \times 76 \times 980.6$ ergs = $\frac{1.013 + 10^6}{10^7}$ joules.

* See page 135.

Thus

$$\left[\left(\frac{\partial E}{\partial \pi}\right)_{T.e}\right]_\alpha = \left[\left(\frac{\partial E}{\partial \pi}\right)_{T.e}\right]_\beta + \left(\frac{\partial E}{\partial x}\right)_{\pi.T} \times \left(\frac{\partial x}{\partial \pi}\right)_T \tag{7}$$

If this value for $\left[\left(\frac{\partial E}{\partial \pi}\right)_{T.e}\right]_\alpha$ be substituted in (6), we find that

$$\triangle v = \left(\frac{\partial E}{\partial x}\right)_{\pi.T} \times \left(\frac{\partial x}{\partial \pi}\right)_T \tag{8}$$

This method was employed by us to find the value for $\triangle v$ of thallous sulphate at 30.00°C.[122] The fictitious volume change was found to be −0.0490 cc/gm., as against −0.0492 cc/gm., the result obtained by the first electrical method.

Let us again turn to Braun's Law and the question of its experimental verification. Now that we have become acquainted with several methods which enable us to determine very accurately the values for $(\partial x/\partial \pi)_T$; $(\partial x/\partial T)_\pi$, Q and $\triangle v$, let us carry out a proof in a specific case, say the system meta-dinitro-benzene-ethyl acetate[123] at 30.00°C, one which is composed of two non-electrolytes. I will first calculate the value for Q from Braun's Law. Then I will compare this calculated value with the result obtained from the direct experimental determination of the fictitious heat of solution of meta-dinitro benzene in ethyl acetate at 30.00°C. If the fictitious heat of solution is to be expressed in gram calories, it is necessary to multiply both members of the equation

$$\frac{(\partial x/\partial \pi)_T}{(\partial x/\partial T)_\pi} = -\,T\,\triangle v/Q$$

by 0.2389 (1 joule = 1 volt-coulomb = 0.2389 gm. calories). The accuracy of this conversion factor does not have a pertinent influence here.

From Braun's Law the fictitious heat of solution may be expressed as

$$Q = -\,0.1013 \times 0.2389\,T\,\frac{\triangle v\,(\partial x/\partial T)_\pi}{(x/\partial \pi)_T} \tag{a}$$

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[122] Ernst Cohen and A. L. Th. Moesveld, Zeit. physik. Chem., **105**, 145 (1923).

[123] Ernst Cohen and A. L. Th. Moesveld, Zeit. physik. Chem., **93**, 385 (1919).

Experiment gave the following values

$$(\partial x/\partial T)_\pi = + 0.755 \pm 0.001 \frac{\% \text{ by weight, sum } = 100;}{\text{degree}}$$

$$(\partial x/\partial_\pi)_T = -0.01161 \pm 0.00005 \frac{\% \text{ by weight, sum} = 100;}{\text{atm.}}$$

$$\triangle v = + 0.0442 \pm 0.0001 \text{cc/gm};$$

Substituting these values in (a)

$$Q = 21.07 \pm 0.10 \text{ gram calories/gram}$$

Direct calorimetric experiments gave

$$Q = 21.02 \pm 0.02^5 \text{ gram calories/gram}$$

The agreement is most satisfactory in this case, coming as it does within the limit of probable error which is at least 0.5 per cent.

We can therefore definitely state that an experimental quantitative examination of Braun's Law has demonstrated beyond doubt that this relationship expresses the results of experiment within the probable error of the measurements. The result also provides an extremely satisfactory check upon the accuracy of the methods which were employed for the determination of the different variables in which a large number of natural constants occur.

In this connection I would like to direct your attention to a number of facts of more general significance, which have a special application when the experimental verification of various and sundry thermodynamical relationships is undertaken. While Ernst Cohen and A. L. Th. Moesveld were engaged with the above investigations, an article by H. F. Sill[124] appeared, also dealing with Braun's Law.

Sill chose to verify this law by using a saturated solution of $Ba(OH)_2 . 8H_2O$ at 25°C. He found his results for the fictitious heat of solution to agree within one per cent. of theory. This outcome caused him to say, "The agreement is seen to be excellent." However, closer examination of Sill's work brings to light some startling discrepancies. His value for $(\partial x/\partial \pi)_T$ is erroneous by about seven per cent. His method admits a possible error of twenty per cent. for $\triangle v$, and the uncertainty of his value for Q is considerable. Finally, mistakes of such size have entered into the determination of the value of $(\partial x \ \partial T)_\pi$, that they can hardly be evaluated.

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[124] H. F. Sill, J. A. C. S., 38, 2632 (1916).

It need hardly be added that the final agreement is to be ascribed to the accidental compensation of the several errors and that this work cannot be regarded as an experimental proof of Braun's Law. Cases of this kind, in which attempts are made to verify important thermodynamical relationships, are very numerous in the literature, and I thought it worth while to bring up this example for your enlightenment[125].

The investigations concerning Braun's Law, which have been elucidated here, as well as others, have shown that the prevailing opinion in regard to the influence of external pressure upon solubility is entirely wrong. Thus Rothmund[126] may be quoted as saying, "The few isolated observations concerning the influence of pressure upon solubility prove conclusively that the effect is a very small one. This might be expected in advance in view of the fact that the volume and various other properties of solid and liquid substances vary but little with pressure."

The same opinion is expressed by John Johnston[127], "In general the effect of uniform pressure upon condensed systems in absence of the vapor phase is very small and can be practically ignored in comparison with the influence of changes in concentration and temperature." However, just to mention one case, it was found that the solubility of meta-dinitro-benzene in ethyl acetate at 30.00°C. had decreased from 52.5 to 42 grams per hundred of solvent upon increasing the pressure to 480 atmospheres, a change of about twenty per cent[128].

For the more detailed considerations in this field, the original literature[129] may be consulted.

[125] See also Ernst Cohen and L. H. Bredée, Zeit. physik. Chem., **117**, 143 (1925).

[126] Rothmund, Löslichkeit und Löslichkeits beeinflussung, Leipzig, 1907, p. 81.

[127] John Johnston, Neues Jahrbuch für Mineralogie, 1915, II. p. 89, particularly pages 101 and 108.

[128] See Ernst Cohen, Wilhelma A. T. de Meester, and A. L. Th. Moesveld, Zeit. physik. Chem., **114**, 321 (1924); Ernst Cohen and D. H. Peereboom Voller, *ibid*, **104**, 323 (1923).

[129] Ernst Cohen and A. L. Th. Moesveld, Zeit. physik. Chem., **93**, 385 (1919), in particular paragraph 89.

SEVENTEENTH LECTURE

IN THE previous lectures it has tacitly been assumed that the electrical charge of an ion remained unchanged under the influence of external pressure. It has been conclusively proved by Th. W. Richards and Stull[130] that the first Law of Faraday holds for all temperatures between 20° and 250°. However, there is but one brief reference in the literature concerning the influence of pressure upon this law. Thus Merrill[131] could find no deviations from it exceeding an experimental error of 0.015% at pressures up to one hundred atmospheres.

I[132], therefore, decided to find out whether any variations from this law could be detected in a range of pressures up to 1500 atmospheres. If these were observed, it would mean that it would be necessary to make the corresponding corrections in investigations which had previously been made. Two identical coulometers were constructed and were connected in the same circuit. They were filled with portions of the same solution of silver nitrate. One of the instruments was allowed to remain at atmospheric pressure, while the other was placed under the desired pressure in the compression bomb. After the electrolysis, both coulometers were treated alike, that is, they were washed, dryed, and weighed in exactly the same way. Because of the fact that these coulometers had to meet special requirements for this investigation it seems advisable to describe them in some detail. The methods of manipulation, etc., may be found in the original article.

The coulometer in the pressure bomb had to be specially constructed to prevent the entrance of oil into that part in which electrolysis was to take place. Due to the compressibility of the solution this fact had to be taken into account so as to prevent the infiltration of oil*. Without these precautions it would have been impossible to secure accurate results as the silver deposit would probably have been unsatisfactory and the solution contaminated. These considerations led to the construction of the coulometers illustrated in Fig. 48 and Fig. 49. A platinum wire *P* is fused into the bottom of a glass tube, *A*, which is about 3 cm. in diameter. After the wire has been flattened against the side wall of the tube, the inside is coated with platinum.

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[130] Th. W. Richards and Stull, Zeit. physik. Chem., **42**, 621 (1903).

[131] Merrill, Physical Rev., **10**, 167 (1900).

[132] Ernst Cohen, Zeit. physik. Chem., **84**, 83 (1913).

* The oil used as the compression liquid was found, as the result of special tests, not to act upon the solution of silver nitrate at 30° even after prolonged contact.

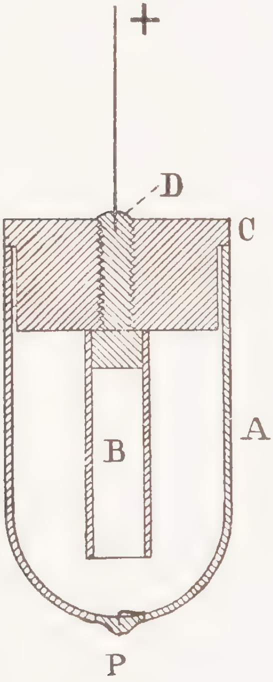

FIG. 48

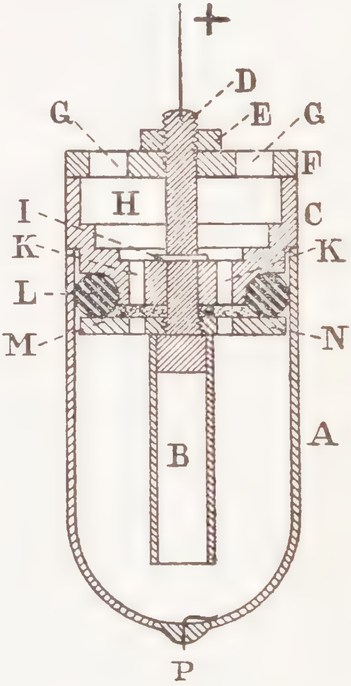

FIG. 49

The apparatus illustrated in Fig. 48 was used for the experiments at ordinary pressures. *C* is a cover of hard rubber which fits loosely upon the glass tube. *D* is a rod of purest mint silver into which a copper wire, the positive pole of the coulometer, is screwed. *B* is a cylindrical piece of silver about two millimeters in thickness, also made of the purest mint silver. It is spring like and may be forced under the cover *C* to *D*. *B* is enclosed in a piece of Schleicher and Schüll filter paper which has been washed with hydrofluoric acid. It is tied carefully in three places by cotton thread, whereupon the resulting capsule is closed at the bottom with some sealing wax. The small apparatus is then placed in a wooden block which has a copper plate at the bottom. The point *P* makes contact with this plate and this, in turn, is soldered to a copper wire which acts as the negative pole.

The coulometer which is to be placed under pressure, Fig. 49, differs from the first only in the fact that it possesses a contrivance which prevents the penetration of oil at high pressures. The hard rubber cover *C* contains a hollow space whose capacity is such that even at the highest pressure all of the oil entering the coulometer may be accommodated by it. If the compressibility coefficient of the silver nitrate solution is assumed to be equal to that of water, 50×10^{-6}, –actually it is somewhat smaller—the highest pressure, 1500 atmospheres, the capacity of *A*, 40 cc., then the space *H* should be able to hold at least $1500\times40\times50\times10^{-6}=3$ cc.

Just as in the previous case *B* and *D* are made of the purest mint silver. In preparing the apparatus for a run, *B* is encased in filter paper as described above, *A* is entirely filled with the solution of silver nitrate and the cover is put into place. The solution accordingly rises through the opening *K* into the hollow space *H*. In order that it remain there, the cover must fit hermetically tight upon the glass tube *A*. For this reason a hard rubber plate *N* is attached below the cover, and between these two on the lower side of the cover is placed a rubber ring or washer *L*. The hard rubber plate *F* with its two openings *G* and *G* is placed upon the cover and the pure silver nut *E* is tightly screwed on *D*. This presses the plate *N* upon the washer which in turn acts as a seal for the coulometer, so that *H* remains filled with the solution. The solution of silver nitrate is subsequently added until the liquid begins to rise in *G* and *G*.

Since the rod *D* passes through the solution and takes part in the electrolysis, particles of silver may drop from *D* during the passage of the current. These may fall through the holes *K* and *K* and may reach the actual working part of the coulometer, causing an error in the final weight of silver deposited. This difficulty is obviated by placing a layer of cotton at *M* to hold back these particles*.

The results, so obtained, at a temperature of 15° are summarized in Table XIII.

TABLE XIII

First Series

	1 atm.		500 atm.		1000 atm.		1500 atm.
A^1	1.5543	A^1	1.4002	A^1	0.6338	A^1	1.6408
B	1.5544	B	1.4002	B	0.6338	B	1.6408

Second Series

	1 atm.		500 atm.		1000 atm.		1500 atm.
A^2	1.6804	A^2	1.4595		not	A^2	1.5096
B	1.6804	B	1.4595		repeated	B	1.5096

The coulometer designated by *A* was always held at ordinary pressures; *B* at higher pressures. A^1 signifies that the coulometer was one of the type illustrated in Fig. 48; A^2 like that in Fig. 49. The numerical data denote the grams of silver deposited. Taking all things into consideration it may be said that the charge of an ion most probably does not change up to 1500 atmospheres, at least not to an extent greater than 1 part in 17000.

Attempts have also been made to determine whether or not the transport number [133] of a cation or an anion changes with external pressure. These experiments have been unsuccessful to date, so that the solution of this problem must be relegated to the future. I shall, therefore, not discuss this subject.

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* The manner in which the coulometer is suspended in the bomb is described in the original article.

[133] R. Gans, Drudes Annalen, 6, 315 (1901).

EIGHTEENTH LECTURE

ONLY after it had been established by van't Hoff that the maximum external work of a chemical reaction could be regarded as a measure of the affinity producing the change, did it become possible to express this value numerically[134]. At the same time van't Hoff also pointed out that the determination of the E.M.F. of a reversible galvanic cell yielded a value for the maximum external work which the chemical process occurring in the cell in question gave at the prevailing temperature and pressure.[135] In other words, every E.M.F. determination of a reversible galvanic cell is also a measure of affinity.

The question regarding the effect of external pressure upon the affinity of a transformation may be answered by studying the influence exerted by pressure upon a reversible cell in which the given reaction is taking place. This effect may be described by the equation,[136]

$$-(\partial E/\partial \pi)_{T.e} = (\partial v/\partial e)_{T.\pi}$$

in which *E* is the E.M.F. of the cell under investigation, π is the external pressure, v is the total volume of the components of the cell and *e* is the quantity of electricity flowing through the cell when one gram equivalent of the substance undergoes a change.

If the cell contains only condensed systems, that is, if it is made up only of liquid and solid phases, the above equation may be reduced to a simpler form.

$$E_\pi - E_o = \pi(v_1 - v_2) \qquad (1)$$

in which v_1 represents the total volume of the components of the cell, and v_2, this volume after 96494 coulombs have been allowed to pass through it. Thus, $(v_1 - v_2)$ is the volume change accompanying the given reaction. Equation (1) may be interpreted to mean that the change in

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[134] Kongl. Svenska Vetenskaps Akad. Handl. **21**, 50 (1886).

[135] An interesting survey of the development of the question of affinity may be found in an article by Ernst Bloch, Isis, 8, (1) 119 (1926).

[136] J. Willard Gibbs, Trans. of the Connecticut Academy of Arts and Sciences, [2], **3**, 508 (1878); P. Duhem, Le Potentiel Thermodynamique et ses applications, Paris, 1886, p. 117; Ernst Cohen and L. R. Sinnige, Zeit. physik. Chem., **67**, 1 (1909); Ernst Cohen and W. Schut, Piezochemie kondensierter Systeme, Leipzig 1919, p. 354. This latter reference contains all the early literature on the subject.

E.M.F. of a reversible cell in absence of the vapor phase is proportional to the change in pressure, as well as to the difference in the volumes of the reactants before and after the passage of a definite quantity of electricity, say 96494 coulombs.

I will now take up the application of this equation to a very simple case[137]. For this purpose let us consider the influence of external pressure upon the Hulett cell with which we have already become acquainted.* It is constructed according to the following diagram:

Metallic Cadmium	Cadmium sulphate solution of any desired concentration	Cadmium amalgam Eight per cent. by weight

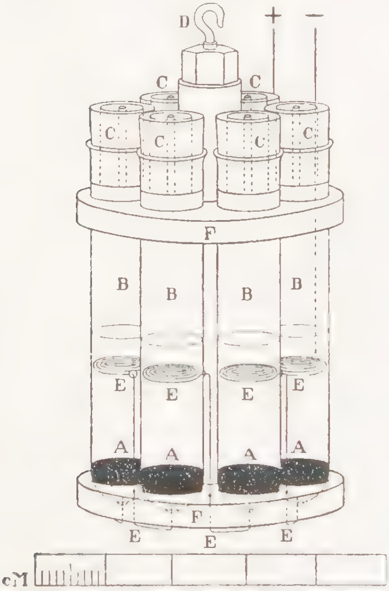

Fig. 50

The reactions which take place when a current is generated are the following:—During the passage of 96494 coulombs through the cell one gram equivalent of cadmium goes into solution. This combines with the sulphate ions present to form cadmium sulphate. At the same time one gram equivalent of cadmium sulphate is decomposed and one gram equivalent of cadmium passes into the amalgam. The reaction consists essentially, then, of the transport of one gram equivalent of cadmium from the cathode to the anode where it dissolves in the amalgam. The E.M.F. of the cell is therefore a measure of the affinity of cadmium for the corresponding amalgam. In order to ascertain the influence of pressure upon affinity, the influence of pressure upon the E.M.F. of the cell at constant temperature must be studied. For this purpose a battery composed, for example, of six elements, Fig. 50, is placed in a compression bomb, which is in a thermostat, and its E.M.F. is measured at various pressures. The results which were obtained at 25.0° are given in Table XIV.[138]

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[137] For more complicated systems see: Ernst Cohen and L. R. Sinnige, Zeit. physik. Chem., **67**, 513 (1909); G. Timofiejew, ibid, **78**, 299 (1911); **86**, 113 (1913); Ernst Cohen and G. de Bruin, Proc. Kon. Akad. van Wetenschappen te Amsterdam, **16**, 164 (1913).

* See page 44.

TABLE XIV

Temperature 25.0° C.

Pressure in Atmospheres	E.M.F. of the battery in volts First Run	Second Run	Average E.M.F. in volts
1	0.30252	0.30276	0.30264
500	0.30811	0.30847	0.30829
1000	0.31390	0.31421	0.31405
1500	0.31973	0.32021	0.31996

The equation which represents the E.M.F. of these cells at 25°C. as a function of the pressure is the following:

$$E_\pi = 50.44 + 0.001855\pi + 0.0000000466\pi^2$$

Thus we find that a 1 atm. pressure

$$\left(\frac{\partial E}{\partial \pi}\right)_{25.0^\circ} = 1.85 \times 10^{-6}\,\frac{\text{volt}}{\text{atm.}}$$

Let us now turn to the determination of $v_1 - v_2$ in equation (1)*. As the cell is to operate reversibly, and consequently the concentration of the reactants must remain constant during the passage of the current, we may picture the whole process as a solution of one gram equivalent of cadmium on the one hand, and the liberation of the same amount with subsequent solution in an infinitely large quantity of amalgam, on the other hand. Since $v_1 - v_2$ represents the change in volume taking place after 96494 coulombs have passed through the cell, it is simply a question of determining the volume change resulting upon the addition of one gram equivalent of cadmium to an infinitely large quantity of the amalgam present in the cell.

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[138] See also unpublished dissertation by J. Casteels, L'influence de la pression sur les forces électromotrices des réactions réversibles, Neufchatel, 1920, p. 41, 45 and 46.

*See page 145.

Two entirely different experimental procedures may be adopted for this purpose, but only the direct method will be described here.[139] The apparatus employed may appropriately be called a dilatometer element, Fig. 51. The two capillaries, *L* and *L*, are fused to the sidearms *A* of the element, but are not directly connected with the latter. The capillaries are partially filled with mercury. Short platinum wires leading from *L* are fused into *A* and are rolled up in a spiral fashion within the sidearms of the cell. The cadmium amalgam, *K*, is placed in the left arm of the tube *A* and upon it, a layer of finely powdered $CdSO_4 . 8/3 H_2O$. The second leg *A* to the right is filled to a height of about 1.5 cm. with crystals of cadmium G which were prepared electrolytically. These are also covered with a layer of finely powdered $CdSO_4 . 8/3 H_2O$. A number of small iron rods *rr* fused in glass tubes are placed upon the crystal layers *HH*. After the apparatus is ready for use these small rods are caused to move up and down by means of a strong electromagnet which is immersed in the thermostat together with the dilatometer element. This keeps the solution well-stirred and fully saturated with cadmium sulphate, as otherwise changes in volume would take place which would cause an error in the results. The tube with the stopcock *E* is fused on at *D*, and a bent glass capillary at *C*. After the apparatus had been filled with a

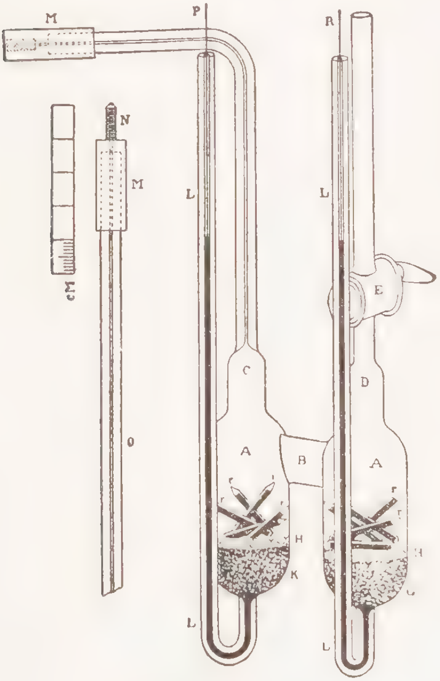

FIG. 51

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[139] For the other method see Ernst Cohen and L. R. Sinnige, Zeit. physik. Chem., **67**, 1 (1909), particularly paragraph 25.

solution of cadmium sulphate saturated at 25.0° C., the air is pumped from the solution, *E* is closed, and the dilatometer element is carefully placed in a regulated thermostat. The capillary *CM* may be lengthened by screwing on the connection *N*. After the temperature equilibrium has been obtained, that is, as soon as the position of the column of liquid in the capillary no longer changes, the dilatometer element is connected with a circuit which also contains two coulometers, a milliammeter, a resistance and a storage battery. By means of a switch the apparatus may be connected with a Poggendorff compensation circuit so that the constancy of the E.M.F. of the element may be checked from time to time.

The actual experiment consists in sending a definite quantity of electricity, as measured by the coulometers, through the apparatus and then ascertaining the resulting volume change. Thus, the level of the meniscus is noted at the beginning of the experiment. The battery, coulometer and dilatometer element are then connected and after a certain time the current is turned off. The level of the meniscus is again read and the volume change is calculated from the weight of mercury which the corresponding part of the capillary holds. The weight of the silver deposited in the coulometer is ascertained from which the number of coulombs which passed through the apparatus may be calculated.

One such experiment yielded the following results:

Decrease in volume	0.0206 cc.
Wt. of silver deposited	1.3458 gms.

The transport of one gram equivalent of cadmium into the amalgam used would therefore correspond to a volume decrease of

$$\frac{107.93}{1.3458} \times 0.0206 = 1.654 \text{ cc.}$$

The first method mentioned above yielded a value of 1.658. Thus, $(v_1 - v_2)$ may be made equal to 1.656 cc.

If, in the equation (1) on page 145, $E\pi - E_0$ be expressed in volts, the expression will assume the following form $E\pi - E_o = 1.05 \times 10^{-3}\pi\ (v_1 - v_2)10^{-3}$ volts, provided π is expressed in atmospheres and $(v_1 - v_2)$ in cubic centimeters. It should be remembered in this connection that one liter-atmosphere = 101.34 volt-coulombs. If, in this equation we substitute for $(v_1 - v_2)$ the experimentally obtained value 1.656 cc., we find

$$\begin{aligned} E\pi - E_o &= 1.05 \times 10^{-3} \times 1.656 \times 10^{-3} \\ &= 1.74 \times 10^{-6} \text{ volts} \end{aligned}$$

whereas, direct pressure experiments gave the value 1.85×10^{-6}*.

The agreement between these results leaves much to be desired; a new investigation in which the compressibility of the substances present in the cell is taken into consideration should be worth while.

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* See page 147.

NINETEENTH LECTURE

YOU are undoubtedly acquainted with the fact that the application of external pressure causes an alteration of both the melting point and the transition temperature of substances. These changes may be treated mathematically by means of the well-known Clapeyron-Clausius equation of which mention had already been made in my ninth lecture.

$$\frac{dT}{dp} = \frac{T\,(v_1 - v_2).}{W}$$

Today we will emphasize more particularly the influence of pressure upon the transition point, and will discuss a number of electrical methods by which we may be able to determine this effect with great accuracy. An apparatus which has appropriately been called a *transition element* will be employed exclusively. This has already been used in determining the transition temperature of tin* and of cadmium** at one atmosphere.

A transition element may be defined broadly as any reversible galvanic cell containing a solid substance which may exist in a number of modifications. By means of such an element the transition temperature may be determined in a manner which will be described later. If the apparatus is to be used for investigations at higher pressures we may call it a *compression transition element.* All such transition elements may conveniently be divided into six classes.

Transition Elements of the First Class

These may be constructed according to the following scheme:

Metal M in the *stable* solid phase	Solution of a salt of the metal M	An Amalgam standard electrode of the metal M

The amalgam electrode must be of such a nature that it suffers no change of condition, such as transition from the heterogeneous to the homogeneous liquid condition, throughout the given temperature and pressure range. In this connection you will recall a previous discussion* where such a change in the nature of the amalgam electrode caused the observer to report the transformation of the metal *M* when such was not the case.

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* See page 42.
** See page 43.

If, at constant pressure, the E.M.F. be plotted as function of the temperature, a break will appear on that E-t curve at the temperature at which the transformation of one modification of the metal to another form takes place. By carrying out these measurements at various pressures the transition temperature will be found. However, as transition elements of the first class have not yet been investigated experimentally, I will not discuss this theoretical possibility any further.

Transition Elements of the Second Class

These may be represented as follows:

Metal M in the *stable* solid phase	Salt solution of the metal *M*	Metal *M* in the *metastable* solid phase.

A cell of this type has actually been employed in the determination of the transition temperature of tin at one atmosphere**. However, it has been impossible to secure exact quantitative data as yet, either at one atmosphere or at higher pressures.

Transition Elements of the Third Class

These cells may be set up according to the following diagram if the transition temperature of the salt *KA* at various pressures is to be determined.

Electrode reversible with respect to the cation K	Saturated solution of the salt *KA* in contact with the solid *stable* phase	Electrode reversible with respect to the anion A.

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[*] See page 43, Figs. 21 and 22.

[**] Mr. Douwes Dekker is at present working on this problem in my laboratory at Utrecht.

In the case of zinc sulphate-heptahydrate the well-known standard cell of Latimer Clark may be employed as the transition element.[140] The type of cell given above then takes the following form:

Zinc-amalgam	Saturated solution of $ZnSO_4.7H_2O$ in contact with the solid phase	Hg_2SO_4H–g

If, at constant pressure and at various temperatures *below* the transition temperature of the *Bodenkörper*, the E.M.F. of such a cell be ascertained, the results may be represented by an equation of this form—

$$E_1 = A_1 + B_1t + C_1t^2 \tag{1}$$

If the same sort of measurements be carried out *above* the transition temperature of the substance, remembering that the *hexahydrate* of zinc sulphate is now the stable *Bodenkörper*, an expression may be obtained which represents at the given pressure the dependency of the E.M.F. of such a cell upon the temperature, as, for instance,

$$E_2 = A_2 + B_2t + C_2t^2 \tag{2}$$

The intersection of (1) and (2) will yield the transition temperature at the given pressure. Thus,

$$t = -\frac{B_2 - B_1}{2\,(C_2 - C_1)} \pm \sqrt{\left[\frac{B_2 - B_1}{2\,(C_2 - C_1)}\right]^2 + \frac{A_1 - A_2}{C_2 - C_1}} \tag{3}$$

TABLE XV
E.M.F. in volts

Temperature	1 atm.	500 atm.	1000 atm.	1500 atm.
25.0°	1.41974	1.42608	1.43223	1.43820
30.0	1.41368	1.42019	1.42604	1.43168
35.0	1.40625	1.41290	1.41892	1.42452
38.0	1.40147	1.40812	1.41427	1.41987
39.5	———	1.40566	1.41183	1.41748
42.0	———	———	1.40772	1.41346
42.5	———	———	———	1.41255
45.0	1.39400	1.39938	1.40479	1.40983
50.0	1.38826	1.39387	1.39920	1.40436
55.0	1.38213	1.38800	1.39338	1.39854

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[140] Ernst Cohen, Zeit. physik. Chem., **25**, 300 (1898); Ernst Cohen, Katsuji Inouye and C. Euwen, ibid, **75**, 1 (1910).

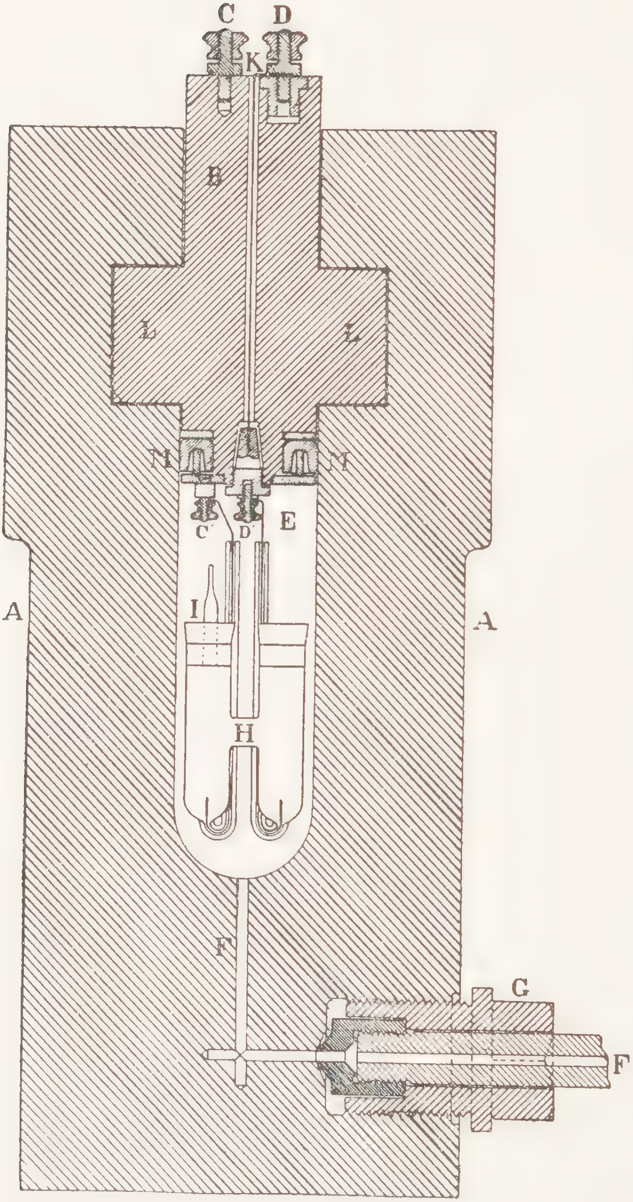

FIG. 52

For this investigation use was made of small Clark cells which were placed in the pressure bomb, Fig. 52. The E.M.F. was measured by the Poggendorff compensation method. Table XV contains the results.

The E.M.F. of the cells which contained the heptahydrate as *Bodenkörper* may be represented as functions of the temperature by the following equations:

At 1 atm. pressure:

$$E_1 = 1.43701 - 0.000221t - 0.0000188t^2 \qquad (A)$$

At 500 atm. pressure:

$$E_{500} = 1.44105 - 0.0000840t - 0.0000206t^2 \qquad (B)$$

At 1000 atm. pressure:

$$E_{1000} = 1.44993 - 0.000263t - 0.0000178t^2 \qquad (C)$$

At 1500 atm. pressure:

$$E_{1500} = 1.46025 - 0.000528t - 0.0000140t^2 \qquad (D)$$

In an entirely analogous manner measurements weer made at 45°, 50° and 55° using cells which contained the hexahydrate as *Bodenkörper*. A similar set of equations was derived.

At 1 atm. pressure:

$$E'_1 = 1.42811 - 0.000407t - 0.0000078t^2 \qquad (E)$$

At 500 atm. pressure:

$$E'_{500} = 1.43277 - 0.000418t - 0.0000072t^2 \qquad (F)$$

At 1000 atm. pressure:

$$E'_{1000} = 1.44475 - 0.000681t - 0.0000046t^2 \qquad (G)$$

At 1500 atm. pressure:

$$E'_{1500} = 1.44331 - 0.000429t - 0.0000070t^2 \qquad (H)$$

If the points of intersection of (A) with (E), (B) with (F), (C) with (G), and (D) with (H), be calculated by means of equation (3)* the desired transition temperatures of the zinc sulphate-heptahydrate to the corresponding hexahydrate at the pressures 1, 500, 1000, 1500 atmospheres may be obtained. The results are summarized in Table XVI.

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* See page 153.

TABLE XVI

Pressure in Atmospheres	Transition Temperature
1	38.12
500	39.96
1000	41.19
1500	42.63

We shall presently have the opportunity to check these results.

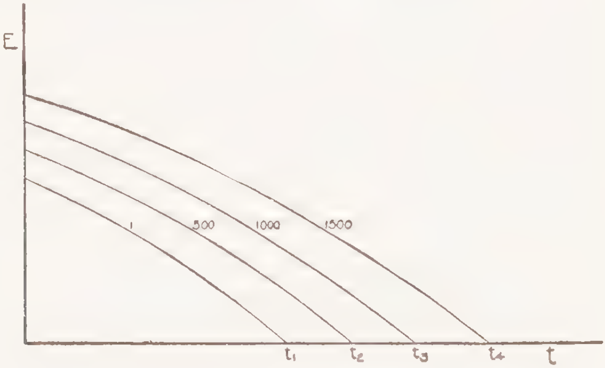

FIG. 53

Transition Elements of the Fourth Class

This type may be divided into two classes, those with, and those without transference. Let us first consider those transition elements without transference. These may be prepared as follows:

Electrode reversible with respect to the cation K	Saturated solution of the salt *KA* in contact with the solid *stable* phase of this salt.	Electrode reversible with respect to the anion A

Such a cell is then connected counter current with another galvanic cell of the following construction:

Electrode reversible with respect to the cation K	Saturated solution of the salt *KA* in contact with the solid *metastable* phase of the salt	Electrode reversible with respect to the anion A

It is clearly evident that both cells must become identical at the transition temperature, and that the total E.M.F. of such a cell will equal zero at that particular temperature. If the E.M.F. of such a cell at constant pressure be plotted, Fig. 53, as a function of the temperature, the point of intersection of the E-t curve with the t-axis will give the transition temperature at the corresponding pressure.

Here also the Clark cell may be used as the transition element. A cell containing the zinc sulphate-heptahydrate is so connected in a circuit that the direction of current flow from it will oppose that of another cell which contains the hexahydrate as *Bodenkörper.*[141]

Table XVII gives the results.

TABLE XVII
E.M.F. in millivolts

Temperature	1 atm.	500 atm.	1000 atm.	1500 atm
25.0	6.03	7.04	7.92	8.74
30.0	4.16	5.15	5.92	6.58
35.0	1.63	2.72	3.60	4.43
38.0	0.04	1.14	2.12	2.83
39.5	—	0.25	1.18	1.98
42.0	—	—	−0.12	0.52
42.5	—	—	—	0.22

The following equations describe the above data:

$$E_1 = 7.86 + 0.1840t - 0.01025t^2$$

$$\text{Thus } t_1 = 38.10°\text{C}.$$

$$E_{500} = 10.84 + 0.048t - 0.00800t^2$$

$$t_{500} = 39.90°\text{C}.$$

$$E_{1000} = 12.29 + 0.0083t - 0.00733t^2$$

$$t_{1000} = 41.35°\text{C}.$$

Lastly,

$$E_{1500} = 12.70 + 0.036t - 0.00778t^2$$

$$t_{1500} = 42.80°\text{C}.$$

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[141] van't Hoff, Vorlesungen über Bildung und Spaltung von Doppelsalzen, Leipzig, 1897, p. 19; Ernst Cohen, Katsuji Inouye and C. Euwen, Zeit. physik. Chem., **75**, 1 (1910), particularly paragraph 36.

A comparison of the data in Table XVI with these results on the transition temperature of this substance at various pressures will show that the agreement is most satisfactory. Transition cells of the fourth class *with transference* [142] are represented as follows:

Reversible Electrode	Saturated solution of the salt KA in contact with the *stable* solid	Saturated solution of the salt KA in contact with the *metastable* solid	Reversible Electrode

Depending upon conditions the electrodes may be reversible with respect to either the anion or cation. Thus, in the case of the transition of zinc sulphate-heptahydrate, either zinc amalgam or mercurous sulphate-mercury electrodes may be chosen. If the transition temperature of Glauber's salt, $Na_2SO_4 \cdot 10\ H_2O$, which, as you know, changes to the anhydrous form at 32.4°C. is to be determined, the transition cell takes the following form:

$Hg-Hg_2SO_4$	Saturated solution of $Na_2SO_4 \cdot 10\ H_2O$ in contact with solid $Na_2SO_4 \cdot 10\ H_2O$	Saturated solution of Na_2SO_4 in contact with solid Na_2SO_4	Hg_2SO_4-Hg

The transition point lies at the temperature at which the E.M.F. of the cell becomes zero.

For Glauber's salt the following results were obtained

$t =$	28.2°	30.2	32.7
$E =$	5.2	2.9	−0.5 millivolts

These figures may be represented by the equation

$$E = -2.05 + 1.571t - 0.0466t^2$$

from which the transition temperature is found to be at

$$t = 32.4°C.$$

as compared with the value 32.38°C. as determined by other methods.[143] Up to the present time no experiments have been conducted upon cells of this variety at higher pressures.

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[142] Ernst Cohen, Zeit. physik. Chem., **14**, 53 (1894); Ernst Cohen and Georg Bredig, ibid, **14**, 535 (1894), particularly page 544.

Let us next consider the

Transition Elements of the Fifth Class

which are constructed, in general, according to the following diagram

Reversible Electrode	Saturated solution of the salt KA in contact with the *stable* solid phase of this salt	Unsaturated solution of the salt KA. *No* solid phase present	Reversible Electrode

Here also the electrodes may be reversible with respect to either the anion or cation.

Glauber's salt[144] may again be chosen to illustrate this class. The cell was made up according to the following diagram:

$Hg - Hg_2SO_4$	Saturated solution of $Na_2SO_4 . 10\ H_2O$ in contact with solid $Na_2SO_4 . 10\ H_2O$	Dilute solution of $Na_2SO_4 . 10\ H_2O$. *No* solid present	$Hg_2SO_4 - Hg$

Cells were subjected to investigation in which the concentration of the dilute solution varied. In Cell I it was made 1 N, in cell II, 0.5 N, in cell III, 0.25 N. If the values for the E.M.F. of such cells at constant pressure be plotted on Cartesian coordinate paper as functions of the temperature, so that the ordinates represent the E.M.F., and the abscissae the temperatures the E-t curves will show a distinct break at the transition temperature. The E.M.F. of such a cell is dependent upon the solubility of the stable solid phase of the salt KA. Consequently the temperature coefficient of the E.M.F. will also be a function of the temperature coefficient of the solubility. As you know, the latter suffers a sudden change at the transition temperature. However, not the solubility or the E.M.F. as such. Therefore, the temperature coefficient of the E.M.F. must undergo a sudden change at the transition temperature, that is, the E-t curve will show a break at this point.

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[143] Th. W. Richards and Wells, Zeit. physik. Chem., **43**, 465 (1903); also Proc. Am. Acad. of Arts and Sciences, **38**, 481 (1902).

[144] Ernst Cohen and Georg Bredig, Zeit. physik. Chem., **14**, 535 (1894); van't Hoff, Ernst Cohen and Georg Bredig, ibid, **16**, 453 (1895).

Up to the present time no experiments have been conducted upon cells of this variety at higher pressures. At one atmosphere the following values for the E.M.F. in millivolts were found at the given temperatures employing the Glauber salt cells mentioned above:

Cell I—using a 1 N. sodium sulphate solution—

$t =$	20.1°	25.4°	30.2°	35.0°	40.0°	45.0°	
$E =$	7.2	11.2	16.8	22.2	22.5	23.1	millivolts

Cell II—0.5 N. sodium sulphate solution—

$t =$	20.1°	25.2°	30.1°	35.1°	40.0°	45.0°	
$E =$	14.3	18.7	24.1	28.2	28.6	28.7	millivolts

Cell III—0.25 N. sodium sulphate solution—

$t =$	20.1°	25.1°	30.0°	35.0°	40.1°	45.0°	
$E =$	21.1	25.7	31.4	35.8	36.7	37.1	millivolts

The E.M.F. of these cells may be represented as function of the temperature by equations of this type: $E_1 = A_1 + B_1t + C_1t^2$—for temperatures between 35°–45° and $E_2 = A_2 + B_2t + C_2t^2$—for temperatures between 20°–30°. Applying equation (3)*, the transition temperature t_0, of Glauber's salt may be calculated.

The equations are found to be

For Cell I

$$E_2 = 12.8 - 1.097t + 0.0407t^2$$
$$E_1 = 28.50 - 0.39t + 0.006t^2$$

from which

$$t_0 = 33.8°C.$$

For Cell II

$$E_2 = 10.12 - 0.297t + 0.0253t^2$$
$$E_1 = 16.63 + 0.548t - 0.00622t^2$$
$$t_0 = 33.0°C.$$

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* See page 153.

For Cell III

$E_2 = 15.00 - 0.190t + 0.0245t^2$
$E_1 = 16.32 + 0.889t - 0.0095t^2$
$t_o = 32.9° \text{ C.}$

A better agreement would undoubtedly have been achieved had the number of observations from which the respective curves were derived been greater.

Investigations at higher pressures have not yet been carried out on transition elements of this kind.

In conclusion let me say that *Transition Elements of the Sixth Class* have not, as yet, been realized experimentally. Such a transition element is to contain a depolarizer which possesses a transition point.

TWENTIETH LECTURE

IN THIS lecture I will discuss the influence which external pressure exerts upon diffusion velocity.

A more thorough knowledge of this effect is desirable not alone because of its bearing upon certain geological problems, but also for the solution of a number of problems involving molecular theory. According to Einstein[145] the equation

$$D = \frac{RT}{N} B$$

may be applied, in which D represents the coefficient of diffusion of the dissolved substance, R the gas constant, T the absolute temperature, N Avagadro's number, and B the mobility of the particles of the solute expressed in terms of the distance through which a molecule moves in a given solvent in unit time when a unit force acts upon it.

Thus diffusion measurements offer a direct method for the determination of molecular mobility, a quantity which is dependent upon the forces at play between the molecules and which change if the condition of the medium in which diffusion is taking place is altered. The simplest change which a medium may suffer is undoubtedly compression; this will cause the distances between the molecules to decrease, while the kinetic energy remains constant. Considered from this point of view the study of the influence of external pressure upon diffusion is highly interesting.

In an article published some years ago by Ernst Cohen and H. R. Bruins[146] it was pointed out that diffusion constants which had previously been determined experimentally at one atmosphere pressure, revealed some startling differences. Due to the great experimental difficulties attendant upon such determinations this might have been expected, but in some cases values had been given for one and the same substance under presumably similar external conditions which differ from one another by 5, 10 and even as high as 60 per cent. In this same article a method was outlined which permitted the determination of the diffusion coefficient in any solvent and at various temperatures with an accuracy of approximately 0.3 per cent. As this method does not lend itself to studies at higher pressures we shall not take it up here, but turn to another procedure[147] by which we may measure accurately the diffusion coefficient, within certain limits, at any desired temperature and pressure. This method has to do with the determination of the velocity of diffusion of metals in mercury.

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[145] Ann d. Physik. (4), **17**, 549 (1905); **19**, 371 (1906); Zeit. Elecktrochem, **14**, 235 (1908).

[146] Zeit. physik. Chem., **103**, 349 (1923).

Let us first consider how the diffusion coefficient may be ascertained in such a case at ordinary pressures. In principle, this procedure was described more than thirty years ago by Des Coudres.[148] It is based on the following considerations:—

A definite amount of a metal is brought by electrolysis of a solution of one of its salts upon the surface of a column of mercury, which may be considered as infinitely long, and which is used as the cathode. The metal is allowed to diffuse. The velocity of diffusion is measured in that, at definite intervals subsequent to electrolysis, the potential difference is determined between the surface of the mercury, which has now become an extremely dilute amalgam, and a constant electrode, which is reversible with respect to the diffusing metal. If only very minute quantities of the metal, in our case cadmium, be brought into the mercury—in all of the experiments to be described this quantity never exceeded sixty milligrams of cadmium per hundred grams of mercury—then the diffusion coefficient, so determined, may be considered as the true one at this temperature.[149]

The diffusiometer is pictured in Fig. 54. It consists of a glass cylinder whose cylindrical form was carefully controlled for that part of it which was used. The diameter was ascertained by cathetometric measurement of the height of a carefully weighed quantity of mercury. In the container is placed a column of mercury of such a height, about 3 cm. that for our purposes it could be considered as infinitely long. An aqueous solution of cadmium sulphate is poured upon the mercury. *Am* represents a constant electrode against which the potential of the mercury surface, the dilute amalgam, may be measured during diffusion. *Am* is a small glass container filled with a cadmium amalgam, which must be heterogeneous at the temperature of the experiment, 20°C. In the experiments to be described a ten per cent amalgam was employed. *Me* is a rod of pure cadmium, which is used as the anode during electrolysis. Both *Am* and *Me* are connected with the hard rubber stopper *S*, which was fastened to the glass cylinder by means of four ivory screws I. *D*, *E*, and *F* are platinum wires which are in connection with *Am*, *Me* and *Hg*, respectively. They are used to connect the mercury column *Me* and *Am* with the measuring instruments which are diagramed in Fig. 55. The cadmium electrode is encased in hardened filter paper to prevent the falling off of small particles of cadmium during electrolysis.

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[147] Ernst Cohen and H. R. Bruins, Zeit. physik. Chem., **109**, 397 (1924).

[148] Wied. Ann. N. F., **52**, 191 (1884).

[149] Zeit. physik. Chem., **103**, 349 (1923), particularly p. 353.

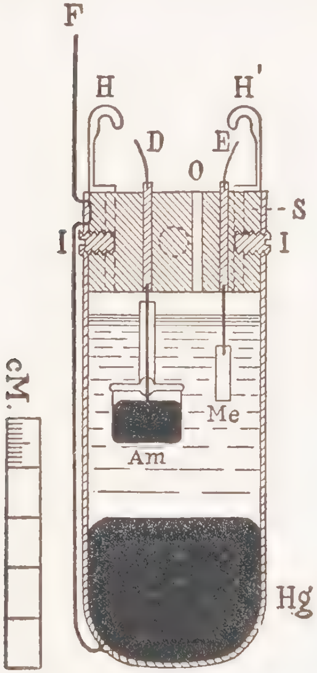

FIG. 54

The actual diffusion experiment then consists of electrolyzing the cadmium sulphate solution for a definite period of time, employing a current of known intensity. *Me* is the anode, *Hg* the cathode. Cadmium is thus deposited at constant rate on the surface of the mercury. After the current has been interrupted, the E.M.F. between *Am* and the surface of the very dilute amalgam which is formed during electrolysis is measured for an indefinite period of time at stated intervals. The original article may be consulted for the details of manipulation.

The question may now be raised as to the manner in which the concentration *c* of cadmium in the surface film of the mercury, at various time intervals, may be deduced from the E.M.F. readings. If this is known, the diffusion coefficient may readily be calculated by means of an equation which has already been derived by Des Coudres.[150]

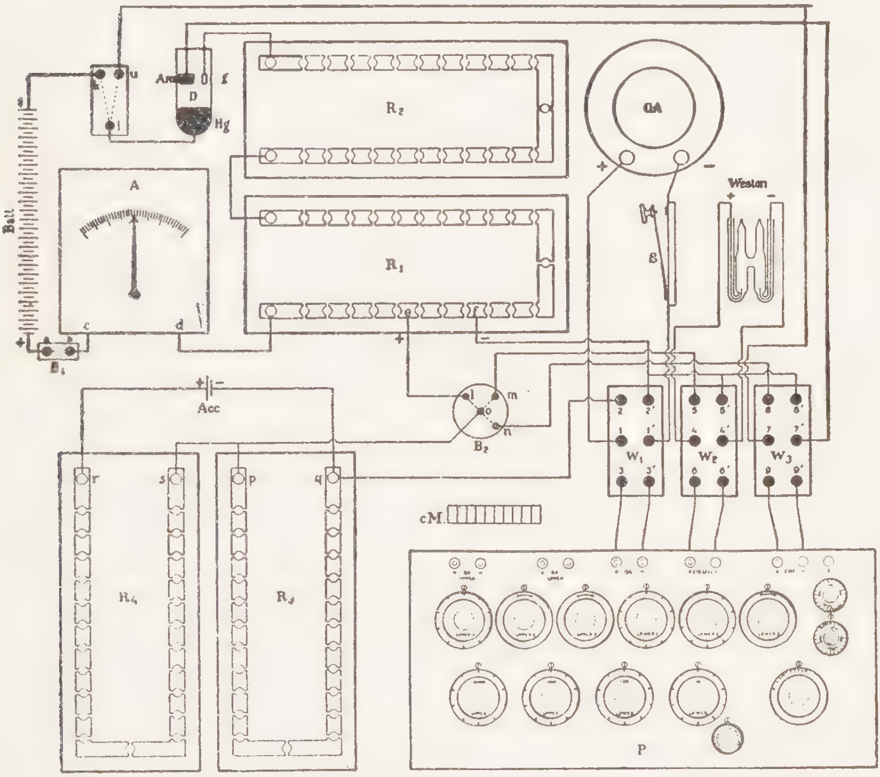

FIG. 55

In order to find *c* the relationship between the E.M.F., *E*, as a function of *c* must be determined experimentally beforehand. For this purpose a known quantity of cadmium is introduced electrolytically into a weighed quantity of mercury, and the E.M.F. between *Am* and the amalgam measured. Of course these preliminary experiments are carried out at the temperature of the diffusion experiments and are repeated with different concentrations of cadmium.

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[150] Wied. Ann. N. F. 52, 1919 (1894).

Since the Nernst equation for the E.M.F. of concentration cells is strictly applicable in this case,[151] because very dilute solutions of cadmium in mercury are employed, the E-c curve may be represented by the equation

$$E = E_o - \frac{RT}{nF}\, \text{l.c.}$$

R represents the gas constant (8.312 volt-coulombs), *T* the absolute temperature of the experiment, *n* the valence of cadmium, and F = 96494 coulombs, E_o a constant which is empirically determined by experiment using cadmium amalgams of varying concentrations. Table XVIII gives the results of such a series of experiments.

TABLE XVIII
Temperature, 20°C.

Weight of Mercury in grams	Time of electrolysis in minutes	J in milliamperes	Weight of cadmium deposited in milligrams	Concentration of cadmium in milligrams per cc. of the amalgam	E in volts	E_o in volts
114.79	180	10.066	63.31^{8}	7.469	0.05778^{5}	0.08316^{1}
114.54	140	10.056	49.19^{7}	5.816	0.06093^{5}	0.08315^{3}
114.53	105	10.041	36.84^{4}	4.356	0.06459^{5}	0.08316^{6}
111.21	100	10.029	35.04^{5}	4.267	0.06486	0.08317
111.87	210	10.029	73.59^{7}	8.908	0.05555^{5}	0.08315^{4}

The average value for E_o is found to be 0.8316.
The equation may now be written as follows:

$$E = 0.08316 - 0.029058 \log c.$$

From this equation the concentration of cadmium in milligrams per cc. of amalgam, as it is expressed in the equation for the calculation of the diffusion constant which we are about to discuss, may be determined, as soon as the E.M.F. between the amalgam formed by diffusion and the electrode *Am* is known.[152] The potential difference is measured during the course of the diffusion by means of the Poggendorff method. Des Coudres' equation from which *D* may be ascertained from values which are capable of experimental measurement, follows:

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[151] Hulett and Delury, J. A. C. S., **30**, 1805 (1908).

[152] Compare Ernst Cohen and H. R. Bruins, Zeit. physik. Chem., **109**, 397 (1924), particularly paragraph 16.

$$\sqrt{D} = \frac{2Jh}{c9\sqrt{\pi}}(\sqrt{t}-\sqrt{t-\theta})$$

J = strength of the current during electrolysis expressed in milliamperes,

h = the electrochemical equivalent of cadmium = 0.005824 milligrams/milliampere,

t = time in seconds from the beginning of the electrolysis to the end of the diffusion,

θ = time in seconds during which the electrolysis took place,

9 = the surface of the mercury in cm^2; in the experiments to be described it was 8.419 cm^2.,

D = coefficient of diffusion in cm^2/sec.

Time is expressed in seconds, current strength in milliamperes, and concentration in milligrams per cc.

The original article may be consulted for the precautions which were taken during the diffusion experiments to prevent disturbances from vibrations of the apparatus and the elimination of temperature changes. Systematic changes which occur if the electrolysis is allowed to take place too quickly or too slowly will also not be discussed here. Of the available data I will choose those summarized in Table XIX, to illustrate the course of a diffusion experiment.

TABLE XIX

Temperature, 20.0°C. J = 3.600 milliamperes

$t-\theta$	E volts	log c	$D \times 10^5$
5400	0.06599^7	0.59062	1.506
6600	0.06677	0.56404	1.510
7200	0.06711	0.55227	1.510
7800	0.06742^7	0.54141	1.508
10800	0.06881	0.49383	1.506
18000	0.07124^5	0.41004	1.510
18900	0.07148^5	0.40178	1.509
28800	0.07370	0.32604	1.510

TABLE XX

Temperature 20.0°C.

Current strength in milliamperes	$D \times 10^5$ cm²/sec.
3.673^5	1.523
3.617^8	1.518
3.600^4	1.509
3.574	1.515
3.395^7	1.525
3.018^8	1.530

The total result $= D^{20.0^\circ\mathrm{C}}_{1\ \mathrm{atm.}} = 1.520 \times 10^{-5}\ \mathrm{cm}^2/\mathrm{sec.}$

Now that we have become acquainted with the manner in which the diffusion constant is ascertained at one atmosphere pressure, let us turn to its determination at higher pressures, say 1500 atmospheres.[153] The same diffusiometer, Fig. 54, may be employed, and it is placed in the compression bomb, Fig. 56. Several factors must here be taken into consideration. The diameter of the column of mercury, whose surface was 8.419 cm² at ordinary pressure, must be corrected for the compressibility of glass, 2.2×10^{-6}

Thus, $9_{1500} = 8.400\ \mathrm{cm}^2$

Furthermore, in calculating the concentration of cadmium c^* in milligrams per cc. of amalgam at high pressures the compressibility of the very dilute amalgam, which is practically the same as that of pure mercury, 4×10^{-6}, must be considered. Thus,

$$\mathrm{d}^{\,20^\circ\mathrm{C.}}_{1500\ \mathrm{atm.}} = 13.626$$

The relationship between *c* and the E.M.F. for amalgams of known concentrations must again be studied beforehand, now at 1500 atmospheres. Then *c* may be calculated, as previously, by ascertaining the E.M.F. between the surface of the mercury and the electrode, *Am*, Fig. 54. The results for known amalgams are given below.

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[153] Ernst Cohen and H. R. Bruins, Zeit. physik. Chem., 109, 422 (1924).

* See page 167.

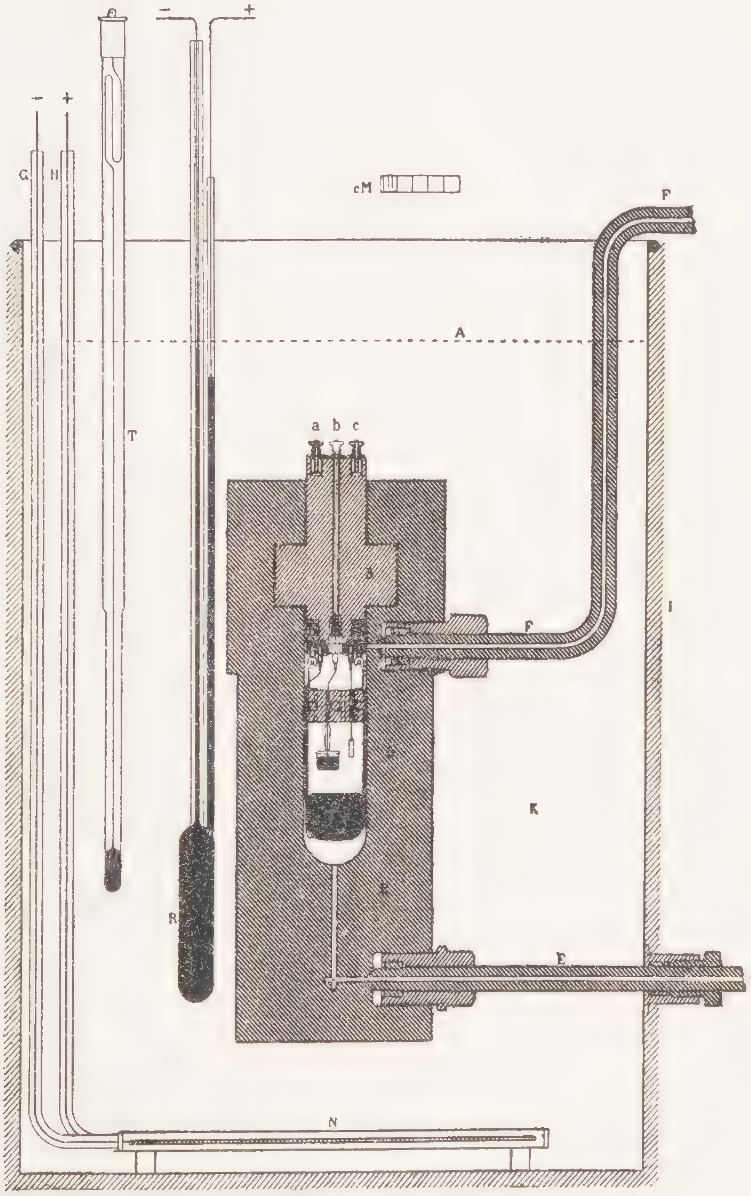

Fig. 56

Table XXI

Temperature 20.0°C., Pressure 1500 atm.

Weight of mercury in grams	Time of electro-lysis in minutes	J in milli-amperes	Weight of cadmium deposited in milligrams	Concentration of cadmium in milligrams per cc. of the amalgam	E in volts	E_0 in volts
114.79	180	10.066	63.31^8	7.469	0.05562	0.08107^4
114.54	140	10.056	49.19^7	5.816	0.05877^5	0.08109^8
114.53	105	10.041	36.84^4	4.356	0.06244	0.08108^6
111.21	100	10.029	35.04^5	4.267	0.06269	0.08107
111.87	210	10.029	73.59^7	8.908	0.05338	0.08105^4

At 1500 atmospheres we find

$$E_{1500} = 0.0810^7 - 0.029058\,(\log c)_{1500}$$

Numerous complications which arose during the course of these experiments are noted in the original article, and reference may be had to the latter for further information. From the available data I will choose but a single table to illustrate such an experiment.

Table XXII

Temperature 20.0°C., J = 4.628^9 milliamperes

$t-\theta$	E volts	log c	$D \times 10^5 \text{cm}^2/\text{sec.}$
5400	0.06050	0.70788	1.454
6600	0.06125^5	0.68190	1.454
7200	0.06160^5	0.66985	1.456
7800	0.06192^7	0.65875	1.455
10800	0.06331	0.61118	1.453
18000	0.06573^5	0.52773	1.455
18900	0.06598	0.51930	1.455
28800	0.06818	0.44359	1.456

Table XXIII

Temperature 20.0°C. Pressure 1500 atmospheres

Current strength in milliamperes	$D\ 10^5\ \text{cm}^2/\text{sec.}$
4.785^6	1.436
4.751^8	1.451
4.737^7	1.432
4.628^0	1.455
4.484^0	1.457
4.435^7	1.442

As the average result we find

$$D^{20.0°C.}_{1500\text{ atm.}} = 1.446 \times 10^{-5}\text{ cm}^2/\text{sec.}$$

and

$$\frac{D_1}{D_{1500}} = \frac{1.520}{1.446} = 1.051$$

Thus, the velocity of diffusion of cadmium in mercury at 20°C. is reduced by five per cent. upon the application of an external pressure of 1500 atmospheres.

TWENTY-FIRST LECTURE

IN CONNECTION with the question concerning the effect of external pressure upon diffusion velocity, which for the specific case of the diffusion of cadmium in mercury has just been answered, let us take up as the last problem of these lectures the question—What is the relationship between diffusion velocity, viscosity and external pressure?

The relation of the diffusion velocity of a substance in a given medium to the latter's viscosity may be ascertained by determining the change which both of these factors undergo upon varying the temperature.[154] It has been found that the velocity of diffusion is inversely proportional to the viscosity, not only where the molecules of the diffusing substance are of a large diameter, but also with possibly slight deviations, where the molecules of the diffusing substance and of the medium are of approximately the same size.

The question may then well be raised—Does this relationship still hold if another variable of condition be chosen as the independent variable?

Since, as we know, the diffusion velocity can be measured accurately at high pressures, we may choose external pressure as the independent variable. The answer to the above question therefore resolved itself into a matter of determining the influence of pressure upon the viscosity of a medium which had previously been employed in ascertaining the effect of this factor upon diffusion velocity.

As we have just studied the influence of pressure in the interval 1–1500 atm. upon the diffusion velocity of cadmium in mercury at 20°C., we may now investigate the effect of external pressure upon the viscosity of mercury at the same temperature.[155]

The usual type of Ostwald viscosimeter may be employed for this purpose, both at 1 and 1500 atm. The difficulty of such measurements under pressure lies in the fact that the flow of the liquid in question through the capillary is only allowed to begin after the apparatus has been permitted to remain in the compression bomb for some

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[154] Ernst Cohen and H. R. Bruins, Zeit. physik. Chem., **103**, 404 (1923).

[155] Ernst Cohen and H. R. Bruins, Zeit. physik. Chem., **114**, 441 (1925).

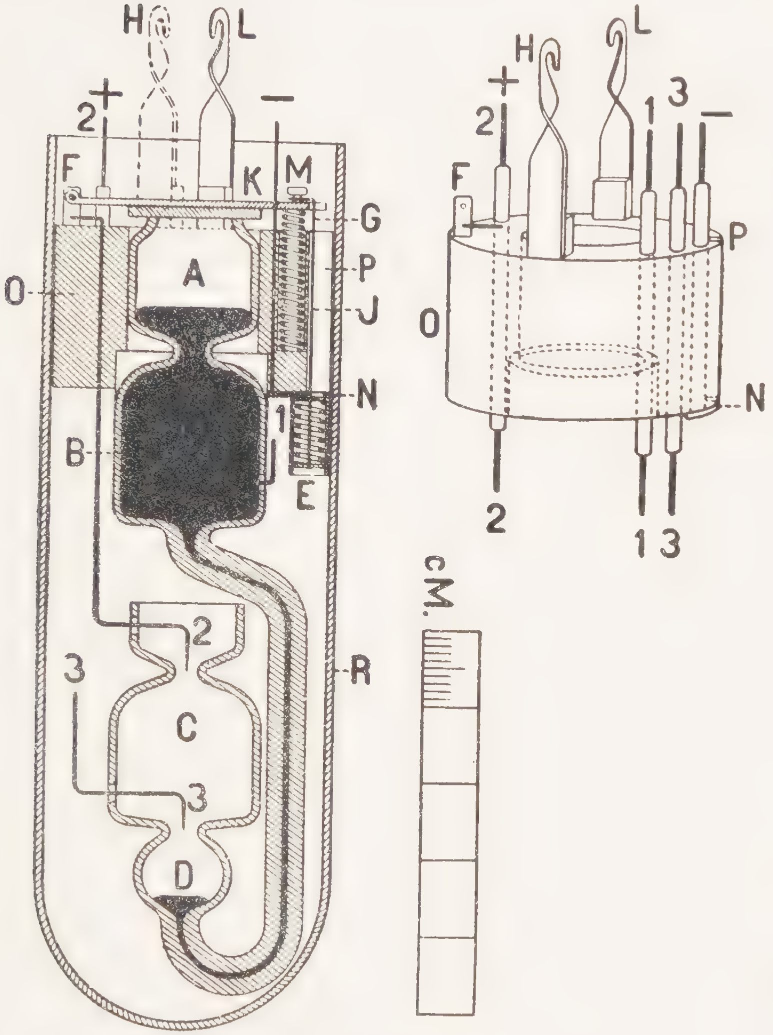

Fig. 57

time so that it will have assumed the temperature of the experiment and the desired pressure. Furthermore, it must be possible to make the measurements of the time of flow of a definite volume of liquid outside of the bomb. This may be accomplished in the following manner. The two containers *B* and *C*, Fig. 57 which we will call bulbs, are made as near alike as possible in respect to both form and capacity. The diameter is 2 cm., the capacity, 4 cc. To prevent the mercury from flowing out immediately after its introduction into the container, or before it has taken on the temperature and pressure of the experiment, the bulb *A* was closed hermetically by means of the cover *K*. The mercury could then begin to flow only when the cover was opened mechanically. This was done by melting, by means of an electric current, a very fine iron wire which held the cover tightly upon the bulb *A*. This caused the cover to open automatically. By means of platinum contacts the exact moment could be ascertained at which the mercury began to flow into the lower bulb as well as when the latter was entirely filled. The contacts were made, for this reason, part of a circuit which contained also an accumulator, a resistance, and a sensitive galvanometer.

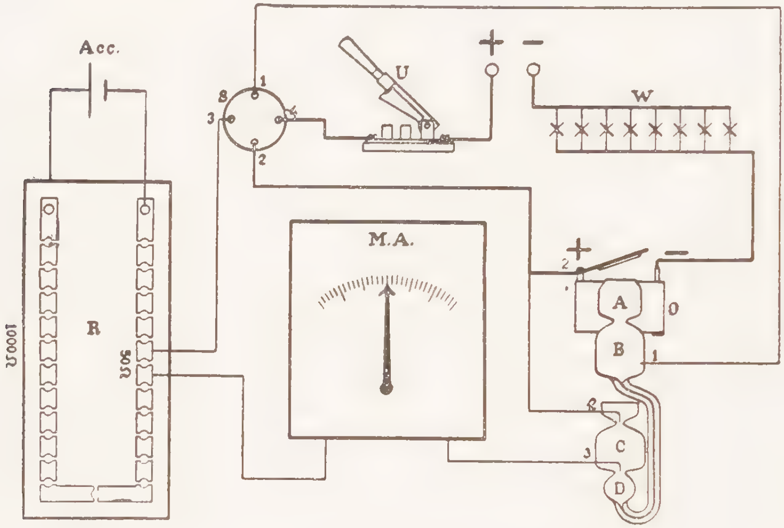

FIG. 58

Although the original publications may be consulted for the various details of manipulations, mention may be made of the fact that the viscosimeter was placed in the cylinder *R* filled with boiled water. The experiments were, in general, executed in the following manner:

The points 2 and 4, Fig. 58, of the switch S are connected. By throwing in *U* the municipal electric current is passed through the wire *J* which is caused to melt. The cover *K* opens and mercury begins to flow through the capillary into the bulb C. In the meantime 2 and 4 are disconnected, and 1 and 3 are joined together. The resistance *R* is so arranged that only a very small part of the current, say 1/20, from the accumulator, which is now the source of electricity, passes through the milliameter *MA*. As soon as the mercury has reached contact 3, thus closing the circuit Acc–R–MA–3–1–S–R–Acc., the needle of the milliameter will show a deflection. The time is noted. The connection between 1 and 3 on the switch *S* is then broken and 2 and 3 are joined. As soon as the bulb *C* has been entirely filled, the mercury in the viscosimeter closes the circuit Acc–R–MA–3–2–S–R–Acc. The pointer of MA will again show a deflection. The time is again noted. The difference between the two time readings gives the desired time of flow.

In order to ascertain how the relative viscosity may be calculated from the time of flow, it will be necessary, first of all, to find out what factors in the Poiseuille equation undergo a change with a variance in pressure. This equation may be stated as follows:

$$\eta = \frac{\pi r^4}{8 l V} pt.$$

in which

η = the absolute viscosity
r = the radius of the capillary
l = the length of the capillary
V = volume of the liquid flowing through
p = the pressure under which the liquid flows
t = the time of flow.

Since we have only to determine the relative viscosity at 1500 atmospheres pressure with respect to the viscosity at one atmosphere, the whole matter resolves itself into determining

$$\frac{\eta_{1500}}{\eta_1} = \frac{(r^4/lV)_{1500}}{(r^4/lV)_1} \cdot \frac{p_{1500}}{p_1} \cdot \frac{t_{1500}}{t_1}.$$

Since r^4 and lv have the same dimensions

$$\frac{(r^4/IV)_{1500}}{(r^4/IV)} = 1.$$

Thus,

$$\frac{\eta_{1500}}{\eta_1} = \frac{p_{1500}}{p_1} \cdot \frac{t_{1500}}{t_1},$$

in which p represents the difference between the hydrostatic pressure of the column of mercury and that of a column of water of equal heighth, as the flow of mercury in the vessel takes place under water.

If we let h = the average heighth of the mercury column, (4.2 cm.), S_{Hg} the density of mercury at the temperature of the experiment, 20°C., S_{H_2O} the density of water under the same conditions, then

$$p = hg\,(S_{Hg} - S_{H_2O}),$$

where g is the acceleration due to gravity.
Thus we find

$$\frac{\eta_{1500}}{\eta_1} = \frac{h_{1500}(S_{Hg} - S_{H_2O})_{1500}}{h_1\,(S_{Hg} - S_{H_2O})_1} \cdot \frac{t_{1500}}{t_1}.$$

The value for h_{1500} h_1 may be determined from the compressibility of the mercury and the average areas of the cross sections of the bulbs *B* and *C*. Due to external pressure, the volume *V* of mercury decreases by the amount $\triangle V$. This quantity is obtained as the product of the external pressure, the volume of the mercury, and its apparent compressibility in glass, β'.

The decrease in the average pressure heighth is thus equivalent to

$$\frac{\triangle V}{\text{average surface}}$$

V = 65.921/13.55 cc. = 4.86 cc., as the weight of mercury in the viscosimeter was 65.921 gm. and its density at 20°C. is 13.55

$$\beta^1 = 1.7.10^{-6};\ \beta_{Hg} = 4.10^{-6};\ \beta_{Glass} = 2.3.10^{-6};$$
$$\Delta V = 1500 \times 1.7 \times 10^{-6} \times 4.86 = 12.4 \times 10^{-3}cc.$$

As the diameter of the bulbs B and C was 2 cm., let us consider their average cross section as equal to 3 cm^2. then

$$\Delta h = -\frac{12.4 \times 10^{-3}}{3.14} = -0.004 \text{ cm., } h = 4.2 \text{ cm.}$$

Thus $$h_{1500}/h_1 = 0.999.$$

At one atmosphere pressure $S_{Hg} = 13.55$
'' 1500 atmospheres '' $S_{Hg} = 13.55 \times 1.006 = 13.63$
'' one atmosphere '' $S_{H_2O} = 0.998$
'' 1500 atmospheres '' $S_{H_2O} = 0.998 \times 1.057 = 1.055$

Consequently

$$\frac{(S_{Hg} - S_{H_2O})_{1500}}{(S_{Hg} - S_{H_2O})_1} = \frac{12.575}{12.552} = 1.002$$

Whence

$$\frac{\eta_{1500}}{\eta_1} = 0.999 \times 1.002 \times \frac{t_{1500}}{t_1} = 1.001 \frac{t_{1500}}{t_1}.$$

In Table XXIV are summarized the results for the viscosity determinations of mercury at one and at 1500 atmospheres pressure.

TABLE XXIV.

Temperature 20.0°C.

one atmosphere pressure			1500 atmospheres pressure		
Experiment number	Time of flow		Experiment number	Time of flow	
1	52 min.	10.8 sec.	8	54 min.	38.8 sec.
2	52 ''	9.0 ''	9	54 ''	38.6 ''
3	52 ''	18.3 ''	10	54 ''	40.2 ''
4	52 ''	10.6 ''	11	54 ''	39.2 ''
5	52 ''	10.8 ''	12	54 ''	35.0 ''
6	52 ''	8.2 ''	13	54 ''	34.0 ''
7	52 ''	12.2 ''	14	54 ''	38.2 ''
Average: 52 min. 11.4 sec. ± 1.3 sec.			Average: 54 min. 37.7 sec. ± 0.9 sec.		

So we find that

$$t_{1500}/t_1 = 1.047 \pm 0.001$$

and

$$\eta_{1500}/\eta_1 = 1.048.$$

Since it has already been found that*

$$D_1/D_{1500} = 1.051$$

we may conclude that within the limits of accuracy of diffusion measurements

$$D_1\eta_1 = D_{1500}\,\eta_{1500}$$

that is, the product of the diffusion velocity and the viscosity is equal to a constant, *independent* of pressure.

Ladies and Gentlemen! In my opening address I pointed out that the purport of these lectures is to fix the student's attention on important points, to acquaint him with the literature which has been published on that particular subject, to point out the way in which certain problems may be studied in connection with the present advance of learning, and, in the last instance, all this is intended not only to make him acquainted with those problems and the methods of solving them, but especially to awaken his love for the study of other topics which have not been treated, and so to fit him for the solution of new problems.

If I have attained this goal in these, my lectures, then will they not have fallen short of their purpose.

FINIS.

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* See page 171.

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